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PHOSPHATE ROCK

A WORLD SURVEY IN SIX VOLUMES

DURING the course of the past four years, the British Sulphur Corporation has carried out a paper survey of phosphate rock deposits throughout the world. All available references on known deposits, exploited and unexploited, have been collected and collated, and this information has been supplemented by visits to major mining areas, and correspondence with mining companies and selling organisations.

The Survey may be purchased in its entirety, or in separate volumes: special rates will apply to libraries and technical institutes.

For further information, write to:—

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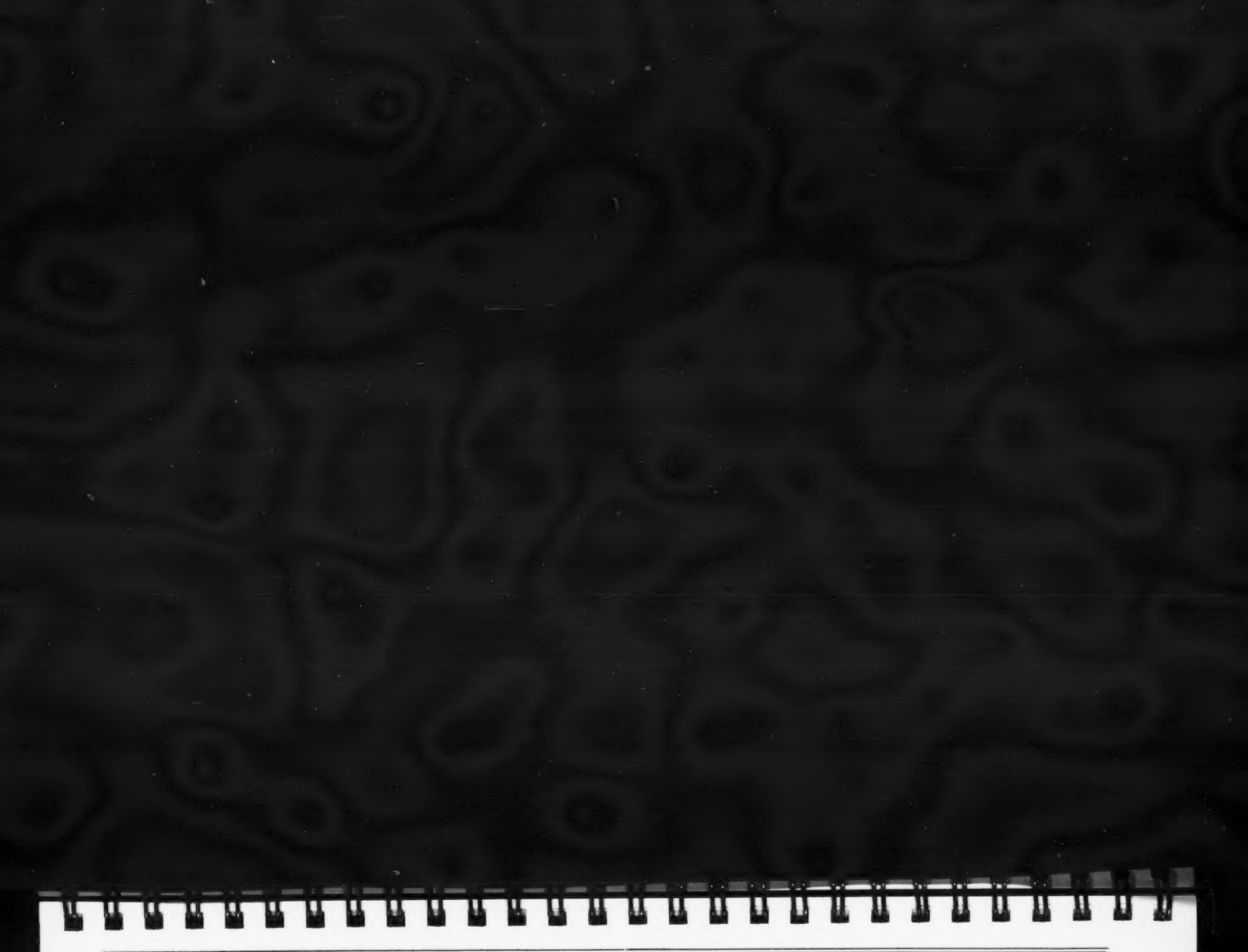


Recovery of Sulphuric Acid and Iron from Waste Pickle Liquor

For many years now acidic liquors, particularly sulphuric acid and hydrochloric acid, have been favoured for economic reasons for removal of oxide scale from steel surfaces. The pickle liquor attacks both scale and descaled steel surfaces at rates depending on its composition and temperature and the type of scale. The by-product in the case of sulphuric acid is ferrous sulphate and in the case of hydrochloric acid, ferrous chloride. Under operating conditions pickle-bath activity is reduced at the higher levels of ferrous sulphate concentration. Determining when pickle liquor is spent and of no further use are economic and technical limitations. Besides their ferrous sulphate content, spent pickle liquors contain greater or lesser amounts of free acid, depending on the pickling technique employed.

When pickling was first carried out, the volume of spent liquor was small and could be run to waste surface water or soak-away. Steel production during recent years, however, has been such that the volume of liquor for disposal has increased tremendously. To-day, in Great Britain it is estimated that sulphuric acid consumed for descaling (in the U.K. about 5% of U.K. sulphuric acid is consumed in pickling and 1% of U.S. sulphuric acid production) produces about 270,000 tons of copperas* by-product ($FeSO_4.7H_2O$) assuming no wastage of acid liquor during pickling. If the spent acid liquor were neutralized by precipitating the iron from solution by lime, then it is estimated that separated wet sludge would amount to over 400,000 tons.

Free Acid Availability

Handling of pickle liquor waste involves not only the liquor from the pickle bath but the acidic and ferruginous liquor carried out of the bath, by drag-out spray and steam dilution (estimated by some to be as high as 40%). Over the years, therefore, a variety of chemical methods of disposal have been developed to render the pickle liquor innocuous prior to dumping, or for removing valuable free acid and contaminant iron salts. Assuming no drag-out losses, with spent liquor containing 40% $FeSO_4$ w/v, the ferrous sulphate is equivalent to 26% H_2SO_4 w/v used up in pickling.

If spent liquor contains 10% w/v of free sulphuric acid, then if this acid can be recovered, the possible saving in acid will be in the ratio of $10/(26+10)=28\%$ of total acid used (W. B. Wragge, The Wire Industry, January, 1950).

Spent Liquor Disposal

Methods of disposal of spent acid pickling liquor are as follows:—

- Direct dumping.
- Sale to chemical industry.
- Neutralisation and precipitation with or without conversion of sludge.
- Crystallisation of surplus iron with free acid recovery by straight cooling, or cooling by vacuum evaporation.
- Evaporation at high temperature or reducing the solubility by chemical means.
- Electrolytic regenerative processes.
- Dialytic acid recovery.

Dumping

Only in one European country is direct dumping of spent liquor (not more than 50% of natural alkalinity of water) into rivers and lakes allowed. If convenient, the liquor can be discharged to sea.

Neutralisation and Precipitation

Neutralising the free acid with alkaline materials and precipitating the iron from solution using milk of lime is practised. The sludge, if small in volume, is accepted by

* Not including copperas from TiO_2 pigment manufacture

sewage plants. Cost of neutralisating and precipitating 10,000 gallons of spent liquor (5% H_2SO_4 w/v 30% $FeSO_4$ w/v) with hydrated lime has been investigated. A weight of 8.18 tons of lime was required and a minimum weight of 23 tons of solids associated with about 58 tons of water as a sludge for disposal was obtained (equivalent to a total sludge volume of 15,000 gallons approx.). Operating costs based on plant providing paddle agitation and employing three men (1950 costs) was £70 a week (Wragge). The amount of sludge produced is too great to be handled by the local sewage works, so additional costs in disposal would be required, or else the sludge is lagooned, and the supernatant liquor drawn off. For handling 50,000 gallons a day of dilute acidic liquor requiring 11lb. hydrated lime per 1,000 gallons, operating costs (1950) were put at £4,000 a year.

Crystallisation

Crystallising methods used in disposal of spent liquor include all the usual methods of reducing solubility of the dissolved salt of the contaminant iron. Such processes depend entirely upon the solubility of copperas or ferrous sulphate at varying degrees of acidity and at varying temperatures. In theory, crystallisation for reclaiming spent sulphuric acid pickle liquor should provide a closed cycle, with no acid wastage. The end product would be either copperas or ferrous sulphate monohydrate. In practice, however, there is acid loss and impurities.

Acid reclaiming systems have been widely used employing intermittent batch recovery on a continuous basis.

Cooling Methods

Straight cooling methods by single stage (to about 15°C using cold water) or by double stage (down to 15°-20°C or less) has been favoured for some time. Separation is by means of centrifuging.

Evaporation

Spraying pickle liquor into the top of an open tank and providing a forced air draft to vapourise some of the water has been developed by Arthur D. Little (American Rolling Mill Company). Spray drying of liquor both with and without prior neutralisation has been referred to in the literature, and continuous processing using a high tower for spent pickle liquor is considered possible.

Construction of a suitable tower poses considerable problems of obtaining sufficient evaporation and cooling. The Zahn " Rollkristaller " is said to overcome the tower problem by employing a rotating inclined drum. Liquor passes down the inside of the drums which has a large number of projections to increase surface area, in a thin stream while an air current is forced through the drum. The crystals are separated from the mother liquor. The whole process operates continuously and a number of units operate successfully in West Germany. Large sizes of drum handle up to 500 gallons an hour.

Vacuum Evaporation

Copperas is extracted from spent pickle liquor by vacuum evaporation, multiple-effect evaporators being favoured. Advantages are that heat transfer occurs under most favourable conditions; both water loss and temperature drop have a combined effect on quantitative crystallisation; and, heat recuperation can be applied with advantage.

Lurgi have developed a plant of the vacuum evaporation type. The first stage of evaporative cooling results from the use of a vacuum pump and barometric condenser, by means of which the temperatures of the order of 25°C can be obtained. Also finding wide acceptance in the oil industry is the Simonson-Mantius vacuum concentrator. With steam pressure of 100lb., the acid can be concentrated to about 63°Be.; in order to reach 66°Be., under 28in. vacuum, hot oil at 500°F is required as a heating medium. Recent forms of the Simonson-Mantius concentrator are supplied with multi-jet steam evacuators capable of producing a vacuum of 29.8in. and giving a 66°Be. acid.

Trials in the U.K. with submerged combustion schemes have shown 90% heat efficiency at the boiling vessel and burner, while waste heat and gaseous effluent can be recuperated to the extent of 70% by the use of a tubular liquor pre-evaporator. This is the Nordac system to which reference is made on Page 4.

Based on makers' figures of 90% efficiency for burner and vessel, and a 70% waste heat recovery, the following costs have been derived (using producer gas at 6d. a therm).

	Batch Pickling	Continuous Strip Pickling
Composition ...	8.1% H_2SO_4 18% $FeSO_4$ w/w	14% H_2SO_4 12% $FeSO_4$ w/w
Fuel cost (per lb. of $FeSO_4$ extracted)	0.40d.	0.35d.

With some wastage, these fuel charges work out at about 10d. to 1s. per ton of pickled strip.

Copperas Disposal

Copperas produced as the result of spent acid disposal and recovered, finds market outlets as follows :—

(a) manufacture of Prussian Blue and iron-base colours
(b) manufacture of certain dyestuffs
(c) gas scrubbing, e.g. Ferrox process
(d) weed-killers
(e) fungicide for timber
(f) precipitating sulphides from leather-trade effluents
(g) treatment and disinfection of sewers
(h) coagulation in sewage plants

With the greatly increased production from the steel industry these outlets are inadequate, hence roasting copperas to convert it to sulphurous and sulphuric gases which are easily convertible to sulphuric acid and iron oxide (easily reduced by sintering in a blast furnace) has been investigated. Copperas is now being roasted to give sulphuric acid at the Grimsby works of British Titan Products and at the Cardiff works of the Imperial Smelting Company of South Wales.

The Ruthner process suggested the use of hydrochloric acid to convert the entire sulphate content of evaporated waste pickle liquor to sulphuric acid and crystallize ferrous chloride. The ferrous chloride is then heated with air and water, producing hydrochloride acid suitable for re-use and iron oxide. Technical feasibility of this process has been proved in pilot-plant operations, but investment costs are high and the end products are such as to be a non-paying recovery system.

Roasting of ferrous sulphate monohydrate (crystallised from pickle liquor) with carbon and air to produce iron oxide and sulphur dioxide and to convert the latter to sulphuric acid has been proposed. This process is more economical than the Ruthner process, but roasting of ferrous sulphate has to be done on a large scale—several hundred tons of acid a day. It has been suggested that where steel mills are congregated in a small area, each could evaporate their waste liquor, re-use mother liquor and send the ferrous sulphate monohydrate crystals to a central roasting plant. Acid produced at the central plant could be shipped back to the steel mills or could be sold to other customers. Iron oxide would also have to be sintered and shipped back to the mills. A notable development in this sector is B.I.S.R.A.'s autoxidation process which gives an economic recovery of sulphuric acid; it is reviewed on Page 11. A similar process is that of Singmasten and Breyer described on Page 16.

In both the above processes, the sulphuric acid recovered is the only credit. Recovery of iron in a ready-to-melt form, rather than iron oxide, would be an advantage since credit for scrap iron or pig iron is reasonable against the value of contained iron in sintered iron oxide.

Performance Data for Crystallizing Acid-recovery Plant*

Plant Maker : Cooling Method :	Kestner Water 20°C(A)	Heastie Brine −5°C	Nordac Brine −4°C	Zahn Brine 0°C	Kestner Water 20°C(E)	Nordac Water 20°C
Spent liquor : H_2SO_4% w/v	10	10	10	7	10	41+1% HCL
$FeSO_4$% w/v						
Recovered mother liquor : $FeSO_4$% w/v	21.15	23	22	29	36	40
Recovered mother liquor (theoretical): $FeSO_4$% w/v	20	7.5	9.5	13.7	19	20
Made-up to orig. bulk : ...	19.8	9.5	10	13.5	18.7	18.3
$FeSO_4$ removed ( ):	13.7	6.4	8.1	11.25	14.6	14.0
$FeSO_4$ removed (%): ...	10.8	16.6	13.9	17.75	21.4	26
Nominal acid saving : ...	44	72	63	61	60	65
	39	39.5	41.5	27.5	30	35

* W. B. Wragge

In an endeavour to plate metallic iron from waste pickle liquor, several electrolytic processes have been developed. In 1955, C. Horner *et. al.*, of Rohm and Haas Company, outlined a method whereby sulphuric acid is produced in a cell utilising an anion exchange membrane. Current efficiency, however, is low and investment and D.C. energy high. Anion membranes have been found to be generally inefficient in concentrated acid solutions.

G. W. Heise *et. al.* in U.S. patent 2,583,098 described an electrolytic plating process which had no membrane. A large part of the iron was oxidised to the ferric state at the anode leaving ferric sulphate in the residual cell liquor. Sulphuric acid is not produced in this process.

To be worthwhile economically an electrolytic cell for ferrous sulphate has to be designed for high efficiency of iron plating and acid formation. With these criteria in mind, Walter Juda, Thomas A. Kirham and Edgardo J. Parsi of Ionics Incorporation have designed a novel three-compartment which is described on Page 19. Another process, that of Siemens and Halske, uses a mercury cell and provides re-usable sulphuric acid at an economic price.

Now being used on a wider scale for separation and purification of acid liquors is dialysis. Although an old-established operation, it has nevertheless been held back commercially because of the poor "life" of membranes. With the introduction of plastic membranes dialysis is proving worthwhile. Two dialysis systems are reviewed on Page 25 and Page 27.

Conclusion

There are then a variety of commercial processes available but the choice of process will of necessity depend on acid regeneration requirements, economics and pollution. The problem of spent acid pickle liquor disposal has no simple solution because of the wide variation in practices in pickling, heating of pickling liquor and differing individual plant conditions. Now that the Rivers Pollution Act has come into force, however, greater attention is being paid to the most economic methods of disposal of spent pickle liquor. The disposal problem facing the steel industry is immense and very serious, but there are good prospects that it can be overcome and in being solved can result not only in removing a source of pollution on land, and in the sea and rivers, but can contribute substantially to the national economy.

Nordac Method of Extraction of Ferrous Sulphate from Pickle Liquor

In recent years attention has been paid to the direct extraction of ferrous sulphate monohydrate from waste pickle liquor. This extraction is desired, firstly, to recover liquor of high activity and secondly to offset the large amount of water which has to be evaporated to maintain the water balance in the pickle tanks. Usually the liquor is evaporated to about 50% w/w acid strength, when practically all the ferrous sulphate separates as monohydrate. The 50% acid can be returned to the pickle lines and the monohydrate can be forwarded to an acid plant. Of two commercial methods of evaporation which have been developed, one is the Nordac process of Nordac Ltd., Uxbridge, Middlesex, England. The other is the Zahn method (see Page 00).

Good Heat Transfer

In the Nordac method, oil or gas is burned, the bottom of the burner being submerged in 50% acid. Hot gases pass through the acid and through the turbulence set up excellent heat-transfer from gas to liquid takes place. The resulting steam and waste fuel gas pass through a series of coils over which waste pickle liquor circulates. To effect some pre-evaporation and recover some heat, air is

drawn over the hot circulating liquor. Concentrated liquor formed flows into the evaporating acid at a controlled rate, to maintain acidity in the evaporator at 50%.

When the liquor is evaporated to 50%, monohydrate separates out and 78% acid (B.O.V.) equivalent to the monohydrate extracted can be added to the evaporator to effect a 10% saving in fuel costs.

The monohydrate and acid as a thin slurry is transferred to a separator, where it is concentrated and pumped to a continuous centrifuge. If of small particle size, the centrifuged monohydrate can retain some 50% acid, so that the final material is not free-flowing but recent improvements in the centrifuging technique have produced a free-flowing material of larger particle size which contains 2.5% acid and 19% $FeSO_4$.

Processing $FeSO_4$ Monohydrate Using Dorr-Oliver Fluid Bed Reactor

A NEW approach to the recovery of iron and sulphur dioxide suitable for sulphuric acid production from steel pickle liquors has been developed by the Dorr-Oliver Company Limited, Croydon, Surrey, England, by employing the Nordac submerged combustion system (see Page 4) in the first stage and a two-compartment fluid reactor in the second. This new process, which is already in operation in the U.K., has considerable economic merit.

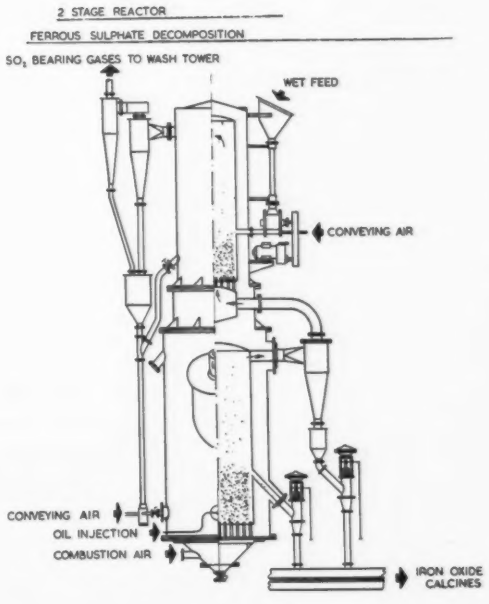
After the pickle liquor has been evaporated to yield some 50% of the acid available in the liquors of commercial concentration ferrous sulphate heptahydrate is converted to monohydrate containing some 7% of moisture and as such is fed to the Dorr-Oliver reactor. Consistency of the cake is such that it would be very difficult to feed this directly into a fluid bed and effectively carry out the decomposition into iron oxides and sulphur dioxide gas. Hot gases leaving the fluid bed compartment below are therefore used to dry out the cake in a fluid bed compartment above and produce a free-flowing powder; in this form the feed is easily led down and blown into the molten bed, where decomposition takes place, as shown in

A rotary filter has been used to filter monohydrate, when a product containing 5% acid and 56% $FeSO_4$ has been obtained.

Continuous Strip Pickling Economics

In continuous strip pickling, it is estimated that the cost of operating the Nordac process is more or less balanced by the value of the acid recovered. Acidity of the whole pickling line can also be increased, with a consequent increase in pickling speed.

At the Trostre works of the Steel Company of Wales Limited a Nordac plant was installed four years ago. This plant can treat the whole output of waste pickle from the continuous strip pickling line. A considerable saving of sulphuric acid has been achieved and the ferrous sulphate monohydrate produced is suitable for production of sulphuric acid.



Dorr-Oliver fluid bed reactor

the accompanying diagram. Much of the waste heat is thereby utilised without the complications of a waste heat boiler.

The waste gas is obtainable at a strength of over 14% SO_2 and per ton of monohydrate cake fed into this reactor, some 0.465 tons of sulphuric acid and 0.4275 tons of iron oxide is recoverable.

In considering the economics of this two-stage system, it should be noted that the average value of monohydrate cake is estimated at £2, although this value does depend on the type of pickle liquor from which it is derived. A 2-ton an hour plant would cost approximately £35,000 and amortization costs on a 10-year period can be estimated at 3s. to 4s. a ton of acid produced. Value of the acid recovered works out at £6 to £7 and that of the iron oxide (Fe_2O_3/Fe_3O_4 or over 60% Fe) is put at about £2 a ton which offsets the operational and amortization costs of the acid plant. The price of the recovered acid compares favourably with that of the general market acid, while at the same time eliminating the difficulties and cost of disposing of waste pickle liquor with no credit return.

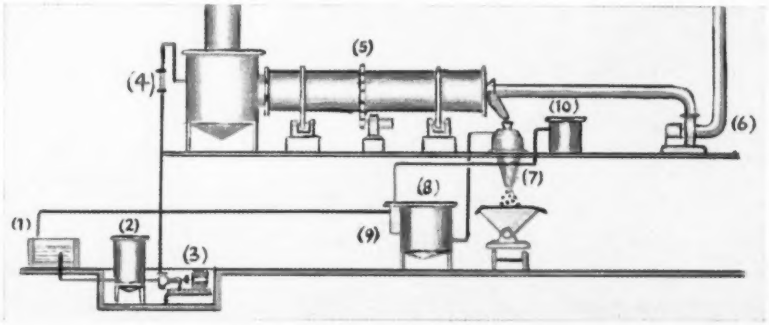
Dorr-Oliver report that the liquor obtained from steel plate pickling is ideal as monohydrate is easily obtained by submerged combustion. It has been noted that it is not quite so easy to obtain a monohydrate of suitable crystal size from titanium liquors because of the way the heptahydrate settles out at a very early stage. Nordac Limited, however, have now succeeded in producing a cake and test work is in progress using this cake as feed.

British Titan Products Limited at their Grimsby Plant already operate successfully a plant of their own design which treats copperas from titanium dioxide manufacture. The new Dorr-Oliver step, however, is reported to offer marked advantages in economies of operation.

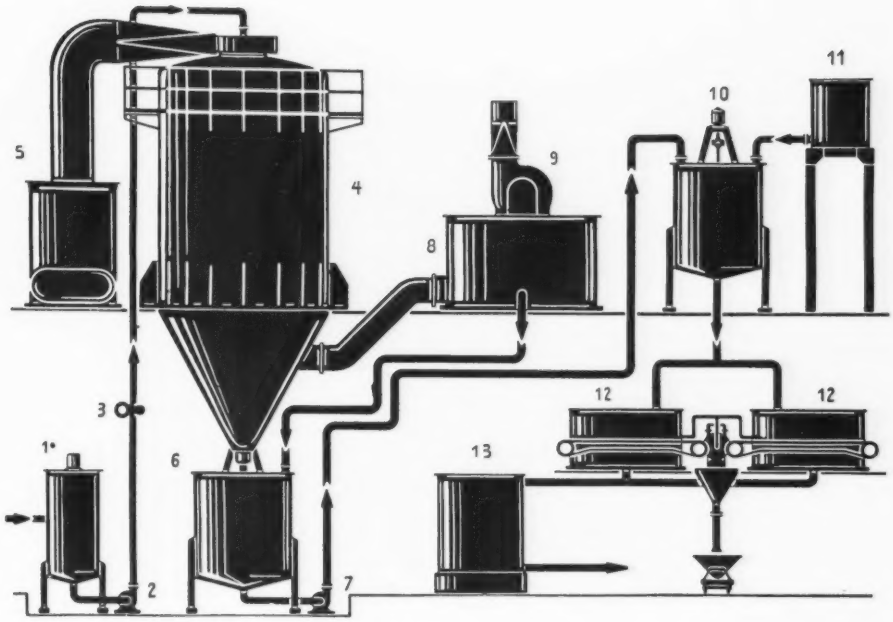
Regeneration of Waste Pickling Liquors using the Zahn Processes

As the result of some 30 years' experience in pickle liquor process development, Zahn Chemie, Hamel/Weser, have evolved a number of recovery processes which cater for a variety of needs. These processes are widely used throughout the world. In the U.S.A. some have been installed through Koppers Company Inc., of Pittsburgh; in the U.K. Zahn pickle liquor plant will shortly be in operation at Richard, Thomas and Baldwin's new plant at Cardiff, South Wales.

Zahn have designed both crystallization plants, where the ferrous sulphate formed from the pickling operations and the sulphuric acid remaining in the bast liquor are separated, the former in the form of crystals by air or vacuum cooling, and evaporation plants producing ferrous sulphate monohydrate as finished product.



Production of $FeSO_4.7H_2O$ using rotary crystallizers



Zahn Monohydrate Process

1. Preliminary vessel
2. Acid pump
3. Flowmeter
4. Evaporation tower
5. Combustion chamber
6. Collection tank
7. Acid pump
8. Separator
9. Exhauster
10. Agitator tank
11. H_2SO_4 measuring tank
12. Filter
13. Collecting tank for regenerated pickle liquor

Monohydrate Process

Production of ferrous sulphate monohydrate $FeSO_4.H_2O$ direct from pickle liquors is effected by spray-evaporation. This process entails:—

- Continuous operation
- Small enrichment of pickling baths (50 to 70 grammes Fe/litre)
- Uniform pickling conditions
- Monohydrate as end product

Pickling solution to be regenerated is received from the pickling tank into the receiving vessel from whence it is continuously pumped through a flowmeter into an evaporation tower, where it is sprayed through nozzles coming into contact with hot gases produced from the combustion chamber (waste gases available from the annealing furnaces can be used). The intimate contact of the pickle liquor with hot gases causes water to be evaporated. The degree of evaporation can be controlled as and when required to suit corresponding changes in the quantity of feed liquor and gases. An exhauster sucks the waste gases saturated with water vapour from the lower part of the tower through the separator to retain acid mist entrained in the waste gases, before discharge of these to atmosphere.

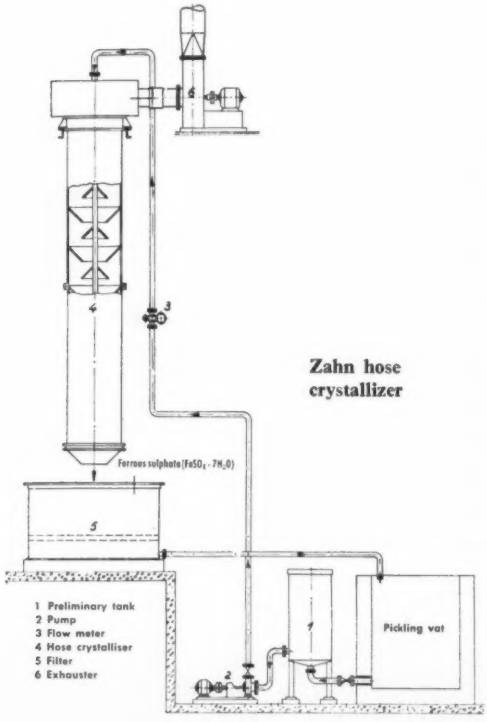
The partially evaporated and consequently highly concentrated pickle liquor leaves the tower through the conical bottom and is colleced in an intermediate tank equipped with an agitataor from where it is pumped to a tank head. Ferrous sulphate monohydrate is precipitated by adding a quantity of fresh sulphuric acid held in a tank, corresponding to the acid strength used in the pickling bath. The precipitated ferrous sulphate is separated by means of vacuum filters, and the mother liquor discharges into the collecting tank, from where it continuously flows back to the pickling tanks, having first been diluted to bring it to the correct pickle liquor concentration.

Production of $FeSO_4.7H_2O$

Using rotary crystallizers, pickle liquor can be regenerated without using water and steam. With special built-in devices the rotary crystallizer provides a very large cooling surface. No moving parts are in contact with the solution.

In this Zahn process, used pickle liquor to be regenerated flows from the pickling tank (1) into the first receiving container (2). A pump (3) continually supplies a certain quantity of the solution via a flowmeter (4) into the rotary crystallizer (5) (designed as a rotating tube) into which cooling air is delivered by fan or blower (6) in counter current to the pickle solution. The solution is thus cooled to a temperature similar to the outside surrounding temperature, when ferrous sulphate separates out. This salt together with the mother liquor flows continually from the rotary crystallizer into a fully automatic centrifuge (7) where instantaneous separation and drying takes place. The dried ferrous sulphate heptahydrate is conveyed to storage. The mother liquor is conveyed to the flow-heater (8) and thence to a mixer (9) where a quantity of fresh sulphuric acid is added from container (10). The regenerated pickling liquor then flows back from the mixer into the pickling tank or tanks.

This process ensures that the pickling bath always maintains the same content of acid and ferrous sulphate and exerts a constant uniform pickling action.



Water Cooled Agitated Crystallizers

Where climatic conditions are such that they do not allow the use of rotary crystallizers, water-cooled crystallizers can be installed. The only difference is that the process is of the batch operation type. Liquor to be regenerated is cooled down by water.

Coolers for Small Capacity

By placing water-cooled cooling elements into the pickling vats or into a special cooling vat, ferrous sulphate is separated quite simply. Crusts of $FeSO_4.7H_2O$ crystals form on the surfaces of the cooling elements which are easily removed.

Dehydration to Monohydrate

As ferrous sulphate heptahydrate cannot be used directly for further processing, that is, by roasting, to convert it into iron oxide with simultaneous production of sulphuric acid from the salt, it must first be dehydrated to the monohydrate ($FeSO_4.H_2O$. A simple and economical method for effecting dehydration developed by Zahn utilizes atomization with instant removal of water from the liquid in the atomized state by intimate contact of the sprayed liquid with hot air or furnace gases. A finely powdered homogenous monohydrate is obtained by a continuous operating process without manual labour.

Caking or crusting of inadequately dehydrated salt is thus avoided.

Novel Hose Crystallizer

Economical for small pickling plant is the Zahn "hose-crystallizer." This has the following advantages:—

- Simple and reliable construction
- Small floor space requirement
- Low operating cost
- High efficiency
- Continuous operation

In this method, a pump sucks off pickling liquor to be regenerated from a tank connected with the pickling vat and conveys it via a flowmeter to the hose crystallizers (see flow diagram). The inner elements of the hose crystallizer are so arranged as to spread the liquor throughout the section of the apparatus. Simultaneously cooling air is sucked in counter-current through the crystallizer. The large surface area of contact between liquor and cooling air results in separation of ferrous sulphate heptahydrate ($FeSO_4.7H_2O$) in the form of crystals. Mother liquor and crystals continuously discharge at the bottom of the hose crystallizer and are separated by filtration. The mother liquor from the filter is returned to the pickling vat. Depending on the throughput of the pickling plant, a quantity of fresh sulphuric acid is added to the mother liquor on its return to the pickling bath.

Notable features of the hose crystallizer include its suitability for continuous operation, shift operation or hourly operation; it can be started and stopped simply by switching on and off and there is no risk of freeze-up so that the hose crystallizer can be installed in the open air.

Basically the Zahn and Nordac processes for the regeneration of sulphuric acid are the same. The main difference between the two processes is in the method of evaporation, and, in the case of the Nordac process, a pre-evaporator can be included if so required.

Zahn vs. Nordac Processes

	Zahn	Nordac with Pre-evaporator	Nordac without Pre-evaporator
B.F. Gas c.f.h. ...	187,500	124,000	184,000
Power consumption ...	140 kw.	188 kw.	198 kw.
Total horsepower ...	209½	301½	323
Water, g.p.h.	1,500	2,500	9,600
Floor area (feet) ...	70 x 70	70 x 50	60 x 50
Drives	15	34	28

Belle Fons Acid Recovery Process for Pickle Liquor

LATEST process for recovery of sulphuric acid from waste pickle liquor is the Belle Fons process. It is already in operation commercially as a 4,000 gal/day unit at the Pittsburgh plant of Hanlon-Gregory Galvanizing Company. The facility was erected by Salem-Brosius Inc., Carnegie, Philadelphia. Cost of the plant is about $100,000. Liquor is concentrated by evaporating water under vacuum, offering these advantages:—

- Equipment, while corrosion-resistant, is less expensive as a lower temperature—130°F as against 190-200°F—is used
- Easy compression and recirculation of the vapour reduce steam requirements and minimize surface needed.

Only intermittent recompression of the low-pressure vapour is necessary since feed pickle liquor, arriving at 160-170°F, gives up sensible heat during the vacuum evaporation. In principle, the Belle Fons process is similar to the Koppers-Zahn process in which liquor is concentrated to the point where $FeSO_4$ monohydrate crystals precipitate and can be separated. The difference, however, is that whereas the Koppers-Zahn process operates at atmospheric pressure, the Belle Fons uses a vacuum.

Operation of the Process

After filtering to remove any solids present, spent pickle liquor is pumped to the top of the evaporator. Flow is controlled by a meter which monitors acid concentration in the stream (normally about 8.5%) and adjusts rate accordingly. At the top of the evaporator, the liquor flows into a recycle stream pumped from the bottom. The combined streams then pass to the evaporator where pressure is reduced to 2-4 p.s.i.a. with a steam-jet ejector. Water vapour is immediately flashed off as the solution passes down through the evaporator tubes as a film.

Vapour formed is drawn off through a metal mesh demister at the bottom of the evaporator, condensed and stored in a rinse tank serving as a source of water for diluting

the final product to pickling concentration. When additional heat input is required, the vapour is compressed with a steam jet and returned to the shell side of the evaporator before it is condensed.

Part of the condensed liquor, at 130°F, and containing about 20 to 21% H_2SO_4 and some $FeSO_4$ crystals is drawn off as recycle and pumped up to the top of the evaporator to mix with feed liquor. The remainder passes to a holding tank where acid concentration is adjusted to 35% by addition of concentrated H_2SO_4. With increased acid concentration more reacted—at about 7% $FeSO_4$ in solution. This equilibrium is independent of temperature in the 150° to 200°F range when acid concentration is about 35%.

As the crystals precipitate in the holding tank, clear acid liquid flows over into a second holding tank. Simultaneously, material is drawn from the bottom of he first tank into an automatic, batch, basket-type centrifuge.

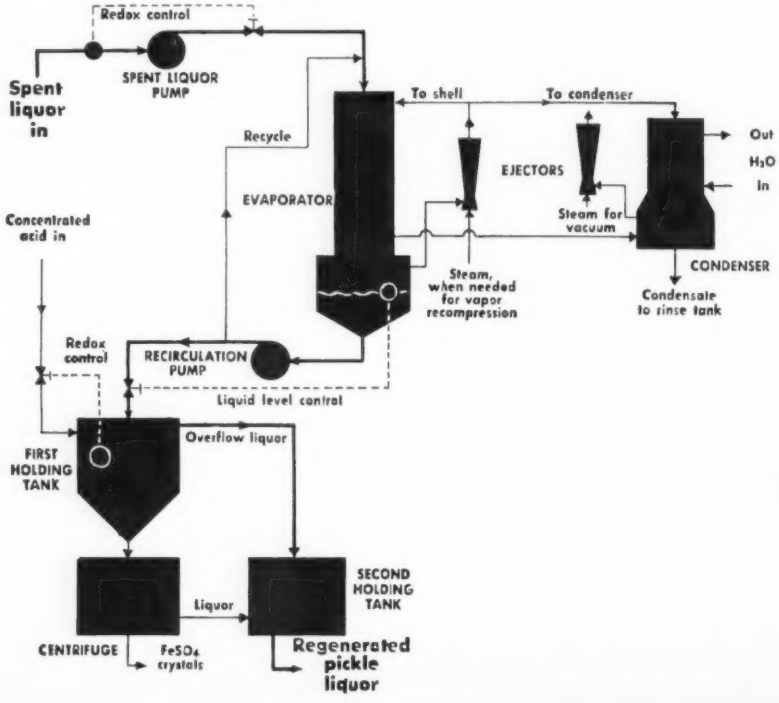
Overflow from the first tank and liquid from the centrifuge which is regenerated acid, collect in the second holding tank. The acid product contains 35% H_2SO_4 and 7% $FeSO_4$, and most of the inhibitors commonly used in pickling. It is diluted to pickling concentration with rinse water recovered from the vapour condenser.

With a small plant such as this one of Hanlon-Gregory Galvanizing Company, the $FeSO_4$ crystals, which contain 3% moisture, are dumped, but in a larger plant processing about 30,000 gallons a day of pickle liquor, roasting and sulphuric acid contacting plants would recover ferric oxide and sulphuric acid from the sulphate crystals.

Plant Requirements

High-alloy steel is used for piping as well as the evaporator, holding tanks and automatic centrifuge. Polyvinyl chloride piping was tried, but its mechanical strength could not be maintained.

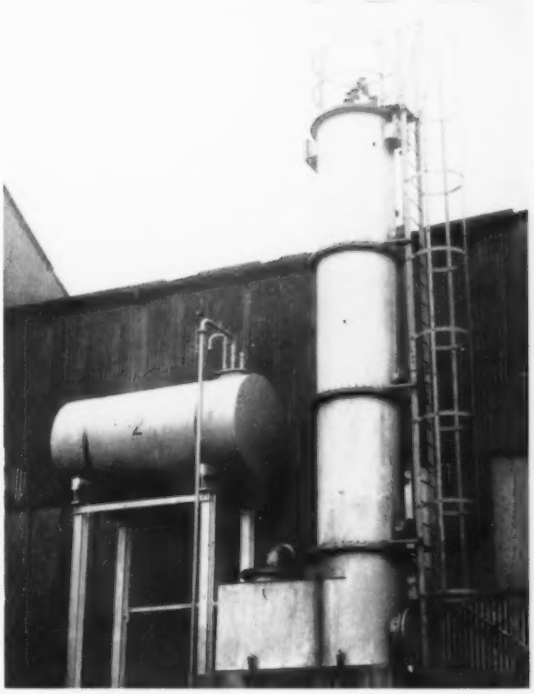
While units up to 18,000 gallons-a-day capacity use ejector recompression, larger units would require turbine compressors for greater steam economy.



Belle Fons process flow diagram

Autoxidation Process for Acid Pickle Liquors

W. Bullough's work at B.I.S.R.A. shows acid for pickling can be produced from waste pickle liquor



Gas-washing tower of pilot plant

INVESTIGATING the problem of dealing with waste pickle liquors, British Iron and Steel Research Association (B.I.S.R.A.) have decided that the best approach, particularly for companies using relatively large amounts of acid such as the steel industry for pickling purposes is to extract ferrous sulphate from the liquor and return the mother liquor containing the unused acid to the pickle tanks. The ferrous sulphate crystals can be converted into acid and iron oxide, thereby achieving maximum recovery in the use of acid as well as solving the disposal problem.

Since extraction of the ferrous sulphate as heptahydrate leaves a mother liquor with a great deal of residual ferrous sulphate and the heptahydrate has to be dried to monohydrate before conversion to acid, the B.I.S.R.A. process extracts the ferrous sulphate as monohydrate by evaporating the waste liquor to about 50 wgt% H_2SO_4 when most of the ferrous sulphate separates as monohydrate. Evaporation is effected by means of a submerged flame using a process developed by Nordac Ltd. The autoxidation process has been chosen for converting the ferrous sulphate to acid as this is most suitable for operation on a small scale.

Investigations in the Laboratory

Sulphur dioxide in aqueous solution can be oxidized with air in the presence of suitable metallic ions. Variables involved using both ferric and manganese catalysts, however, have been studied by B.I.S.R.A. in order to optimize conditions for the autoxidation reaction.

Using a laboratory-scale apparatus, it was found that manganese sulphate was a more efficient catalyst than ferric sulphate. In considering other variables—manganese concen-

FOR the steel industry disposal of waste sulphuric acid pickle liquors has always been a problem. Neutralization of unused acid and precipitation of iron as hydroxide with lime, which has been one solution, is an expensive method, as valuable materials—lime, iron oxide and sulphur—are lost. The B.I.S.R.A. autoxidation process was proved by trials on a scale of 1 ton-a-day of H_2SO_4 to be both practical and economical for a large pickling plant, and at Steel Company of Wales Limited a 17 tons-a-day sulphuric acid from ferrous monohydrate plant was installed by Simon-Carves Limited.

tration, acidity, temperature, oxygen partial pressure, gas/liquid interface area, effect of contaminants on the catalyst and their removal, and effect of circulating the acid with the SO_2 fed into it—it was observed that at a certain acidity, temperature and manganese concentration, the amount of SO_2 converted to acid was roughly proportional to the average oxygen partial pressure in the bubbles, and to the gas/liquid interface area, it was thought use of a temperature increased the conversion efficiency. As reduction in bubble size increases the gas/liquid interface area, it was thought use of a wetting agent would be useful. The majority of wetting agents, however, were found to poison the catalyst. Acetic acid was found to be non-poisonous and decreased bubble size so that a 0.05% addition gave a fourfold increase in efficiency.

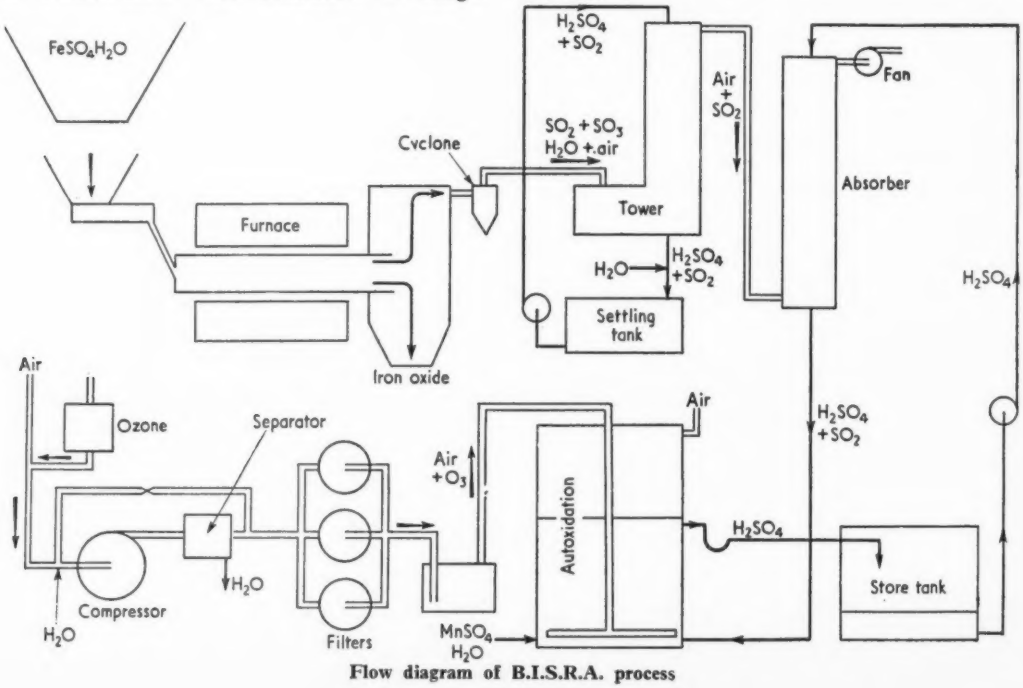
Pilot-Plant Studies

As the laboratories studies proved favourable, the process has been tested on a scale of 1 ton of 100% H_2SO_4 a day. A pilot-plant was therefore designed and erected by Simon-Carves Limited of Cheadle Hulme, Cheshire, in collaboration with B.I.S.R.A. at King's Dock Works of the Steel Company of Wales Limited with financial assistance from all three organisations.

Initial trials showed that if the plant was operated as a single-stage process—compressing and feeding the SO_2 into the autoxidation tank with air—SO_2 corroded the compressor. The plant has therefore been operated as a two-stage process.

Process and Plant

Ferrous sulphate monohydrate as produced by the Nordac process was transferred from a storage hopper to a small hopper, from the bottom of which it was fed into a furnace by a screw conveyor. These pieces of equipment have to be rubber-lined as the monohydrate contains some residual acid. The furnace used in the trial plant consisted of a stainless-steel retort which could be inclined, rotated and heated to 900°C by oil burner placed in a combustion chamber above the retort. On passing down the retort, the monohydrate is converted into iron oxide and a gas containing sulphur dioxide and sulphur trioxide, steam, dust and any air that is drawn through the retort.



Flow diagram of B.I.S.R.A. process

In the early trials, by the time the material had travelled to the hot end of the retort, 95% of the sulphur content had been evolved. As the iron oxide travelled along the cooler end of the retort, it reacted with the SO_3 above it. This reaction continued in the smoke box resulting in a sticky mixture of iron oxide and ferric sulphate having a sulphur content of 7.0%, corresponding to a roasting efficiency of only 80%.

When monohydrate was roasted with a 2% addition of fine coal the retort temperature could be reduced, much less SO_3 was produced and the iron-oxide was free-flowing and contained 0.85% sulphur; this sulphur content corresponding to a roasting efficiency of 98%. On leaving the retort, the iron oxide falls to the bottom of the insulated smoke box and is discharged by means of an automatic flap valve. The hot gas travels up the smoke box at low velocity so as to allow some of the iron-oxide dust to settle, then through a cyclone to extract more dust, and finally along a Pyrex pipe to a gas-washing tower.

Gas Washing

Gas passes up the lined and packed gas-washing tower where it is cleaned, cooled, and some of its acid mist extracted by a downward flow of cool acid. The hot, dusty, and more concentrated acid is cooled, and its dust allowed to settle in a cooling and settling tank; it is then pumped back to the gas-washing tower.

Steam and SO_3 produced in initial trials dissolved in the gas-washing liquor and increased its acidity to a maximum of 20%. The trace of iron-oxide dust which passed through the cyclone dissolved in this acid, forming ferric sulphate which was then reduced to ferrous sulphate by the SO_2 in solution. After stripping of its SO_2, this acid was used for pickling. The amount of acid formed was equivalent to 16% of the sulphur input to the furnace.

Much less SO_3 was produced in later trials, and very dilute acid containing iron-oxide dust was formed in the gas washer; its quantity was equivalent to only 3% of the sulphur input to the furnace.

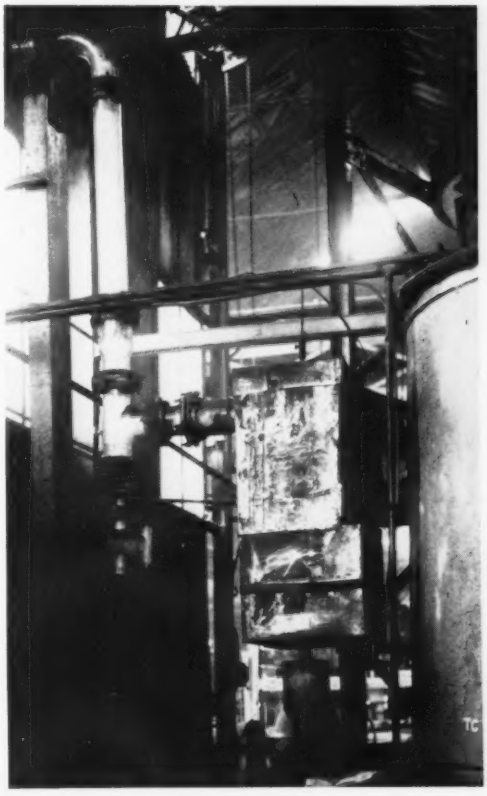
Absorber Tower

Cool, clean gas leaving the gas-washing tower is run to a rubber-lined absorber tower packed with Raschig rings, where it is met by a downward flow of dilute acid containing a trace of manganese sulphate. The gas issuing from the top of the tower contains a very slight trace of SO_2 and is drawn off by means of a fan and discharged to atmosphere; the acid containing the dissolved SO_2 is fed into the bottom of a lined diffusion tank.

It was found that 96 to 98% of the SO_2 dissolved in the autoxidation acid and, moreover, no acid mist could be detected in the gas leaving the absorber.

Compressors and Filters

Air containing a small amount of ozone is compressed by a Nash Hytor compressor, filtered, and delivered to a multiple diffuser mounted in the bottom of the diffusion tank. During trials the pressure drop across the filters



Pyrex cooler and cyclone

remained at 2lb./sq. in. and examination showed that the Nash Hytor compressor had removed all the dust from the air.

Diffusion Tank

Under initial trial conditions of manganese concentration, average SO_2 rate and air rate of 0.02%, 3.4 and 210 cu. ft. respectively and the heat of the reaction, the temperature rose to an average of 45°C. Autoxidation efficiency was more than 99% without use of ozone, until acidity reached 23 wgt%. As acidity increased, an increasing quantity of ozone was necessary. Maximum acidity obtained was 41 wgt%. In later trials, with acidity maintained at 32 wgt%, the furnace was operated at the rate of 0.75 ton/day of H_2SO_4 (i.e., 4.3 cu. ft./min. SO_2).

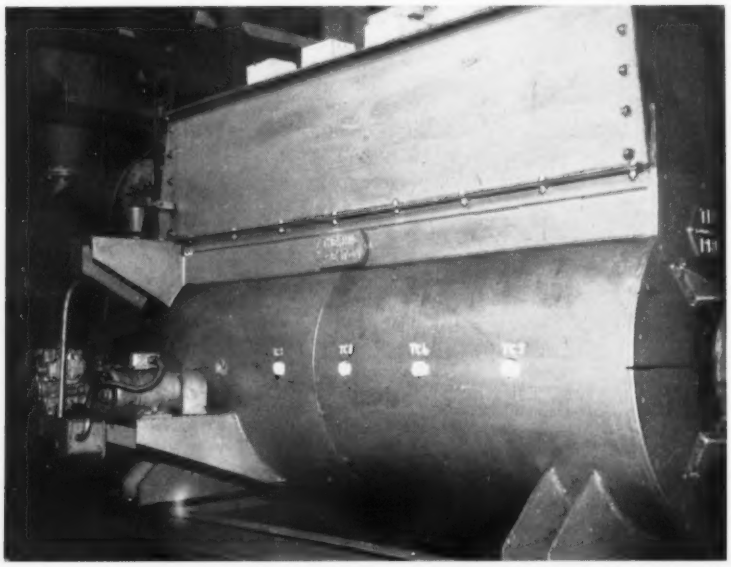
Results indicated that the designed rating of 1 ton/day H_2SO_4 (i.e., 5.7 cu. ft./min. of SO_2) was made at 98.5% efficiency with the ozone rate only 26 g./hr. Increase of SO_2 rate did not cause efficiency to fall off as in the pilot tank rising bubbles circulate the acid within the tank. Reduction in air rate with ozone rate kept constant did not cause efficiency to fall off as rapidly as expected, due to (a) the ozone concentration in the bubbles increasing, (b) smaller bubbles being produced and (c) less SO_2 control on the reaction.

From the diffusion tank acid overflows to a storage tank and is then recirculated to the absorber tower. Water and manganese sulphate can be added to this system to maintain the acidity at a required level, and excess acid delivered to the pickle tanks.

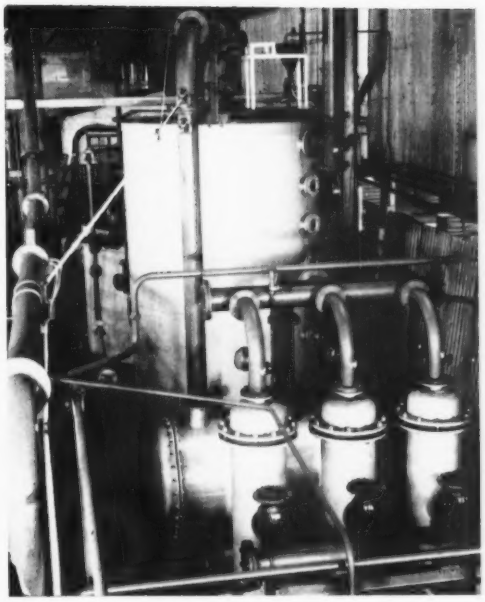
Plant Development

Since the pilot-plant trials showed that the two-stage process could produce pickling-strength acid, a commercial plant to produce 17 tons/day H_2SO_4 from monohydrate was designed by Simon-Carves Ltd. Because of sticking of wet monohydrate the autoxidation plant takes its feed direct from the evaporation plant. An oil-fired, fluidized-bed roaster working under slightly oxidizing conditions and giving a gas containing about 10% SO_2 is used. The gas is suitable for autoxidation and the sulphur content of the iron-oxide is low.

Roaster gas passes through cyclones and a gas-washing tower to remove dust and cool the gas. Since SO_3 is at a minimum, acidity of the tower effluent is low and this can be neutralized together with acid rinse water from the pickling plant. SO_2 is dissolved in 30% acid in an absorber tower and passes to the diffusion tank. Diffuser area is as large as possible to reduce bubble diameter to a minimum. Acid strength is maintained at 30% by adding water and catalyst.



Feed hopper and furnace



Diffusion tank and filters

Cost Analysis of Autoxidation

Costs are based on one ton of 100% H_2SO_4 for a 17 tons/day H_2SO_4 capacity plant, working continuously at 80% of capacity—i.e., 5,000 tons/year.

	Min.	Max.
Fuel oil for roasting @ 10¾d./gal. at 900°C		2.44
at 780°C	2.00	
Electric power for compressor pumps, small motor ozonizer	1.17	1.61
Cooling water: 18,900 gal. @ 3¼d./1,000 gal.	0.3	0.3
Operating personnel 1 operator per shift @ £10/week 1 chargehand @ £12/week shared Total £16/week on 3 shifts ...	0.48	0.48
Depreciation at 10% and interest on capital at 5% of estimated plant cost of £150,000-£200,000 ...	4.5	6.0
Manganese sulphate	0.06	0.12
Maintenance cost	0.75	0.75
	£9.26	£11.70
Less credit for iron-oxide calcine suitable for blast-furnace sinter plant—value about £3/ton of oxide (1 ton H_2SO_4 is equivalent to 0.828 ton of Fe_2O_3)	2.5	2.5
	£6.76	£9.2

Thus assuming ferrous sulphate monohydrate is available at no cost and there is credit for iron-oxide calcine, 30% acid can be prepared from monohydrate by the B.I.S.R.A. autoxidation process on a 17 tons/day 100% H_2SO_4/day scale at a cost of £6 15s.-£9 4s. per ton of 100% H_2SO_4.

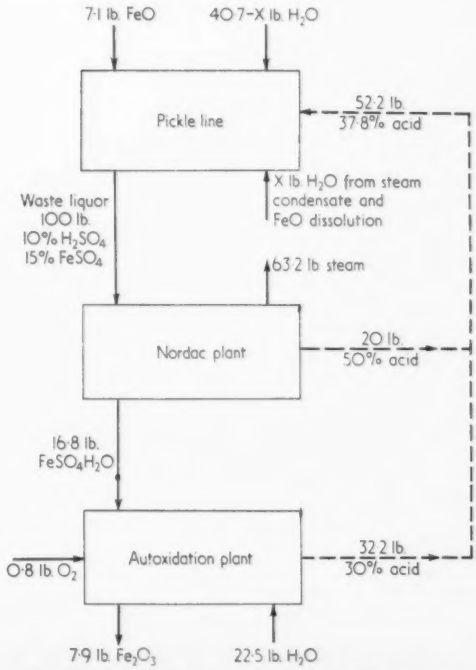
Material Balances

Material balances which might be expected in an integral system using a Nordac evaporation plant are indicated below. In practice some acid has to be added to balance that lost in (a) dragout and spray from the pickle line, (b) condensate in the Nordac plant, and (c) sulphur in the iron oxide and SO_2 lost from the autoxidation plant.

In a typical continuous pickling line system, the make-up acid would be equivalent to about 1.9lb. of H_2SO_4 and X would be about 20lb. per 100lb. of waste liquor. Thus if X is less than 40.7lb. then an autoxidation acid strength of less than 30% would be adequate.

Conclusion

B.I.S.R.A.'s autoxidation process has proved during trials on a scale of 1 ton/day of H_2SO_4 to be practicable and economically justified for a large pickling plant. Used in conjunction with a monohydrate recovery plant the problem of disposal of waste pickle liquor is solved, and the value of acid recovered offsets costs involved.



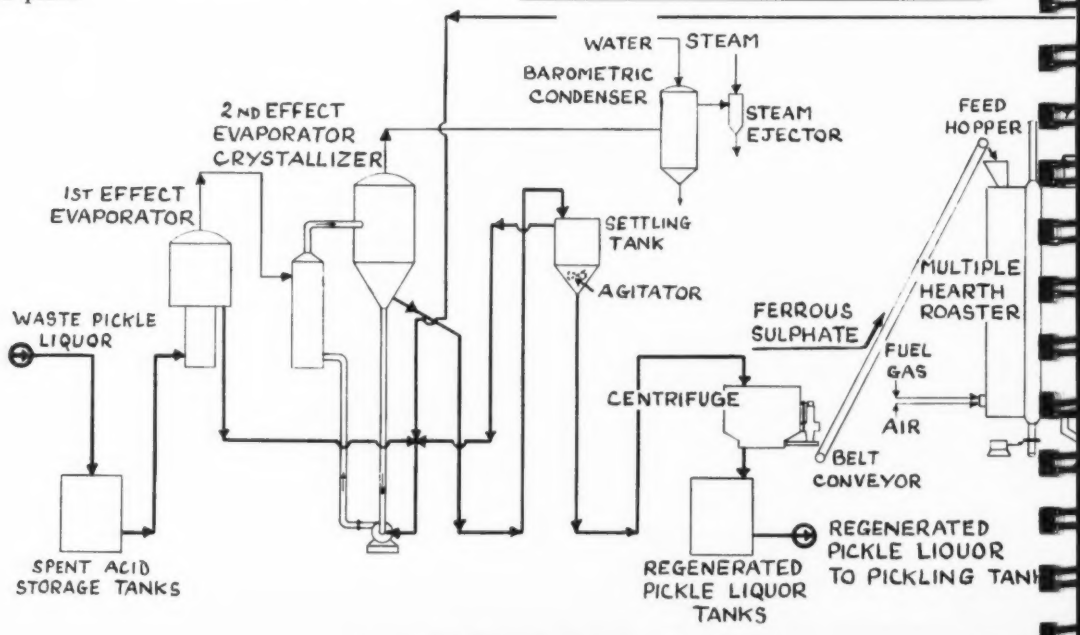
Material balances in a closed-cycle pickling system

Profitable Pickle Liquor Regeneration using the Singmaster and Breyer Process

RECENTLY developed by Singmaster and Breyer of New York is a process which is simple and gives a sulphuric acid regeneration cost of under $15.00 a ton, with a credit of iron oxide. Chemistry of the process is simple, and well tried engineering techniques are employed. In essence the process has three major steps: concentration of pickle liquor and the resultant crystallization of ferrous sulphate monohydrate in a multiple-effect evaporator; roasting of ferrous sulphate monohydrate in a multi-hearth furnace under such conditions that substantially no SO_3 is generated; and the generation of 98% sulphuric acid in a contact acid plant.

Advantages of the Process

- As the process operates under vacuum, and therefore at a low temperature, corrosion problems are minimized
- Vacuum is generated by steam jet and the steam jet apparatus automatically picks up any fumes
- Thermal economy is enhanced by use of heat of dilution of 98% sulphuric acid in the second effect evaporator
- Proper crystal size and shape which is readily filterable and washable, is insured by use of an evaporative crystallizer
- The end product—a 45% sulphuric acid with less than 3% ferrous sulphate can be used for pickling. Diluted to 20% acid, the ferrous sulphate content is under 1-½%
- By addition of small quantities of sulphur-bearing material during roasting, the combination of pickling plant and regeneration plant is completely self-contained with respect to acid requirements



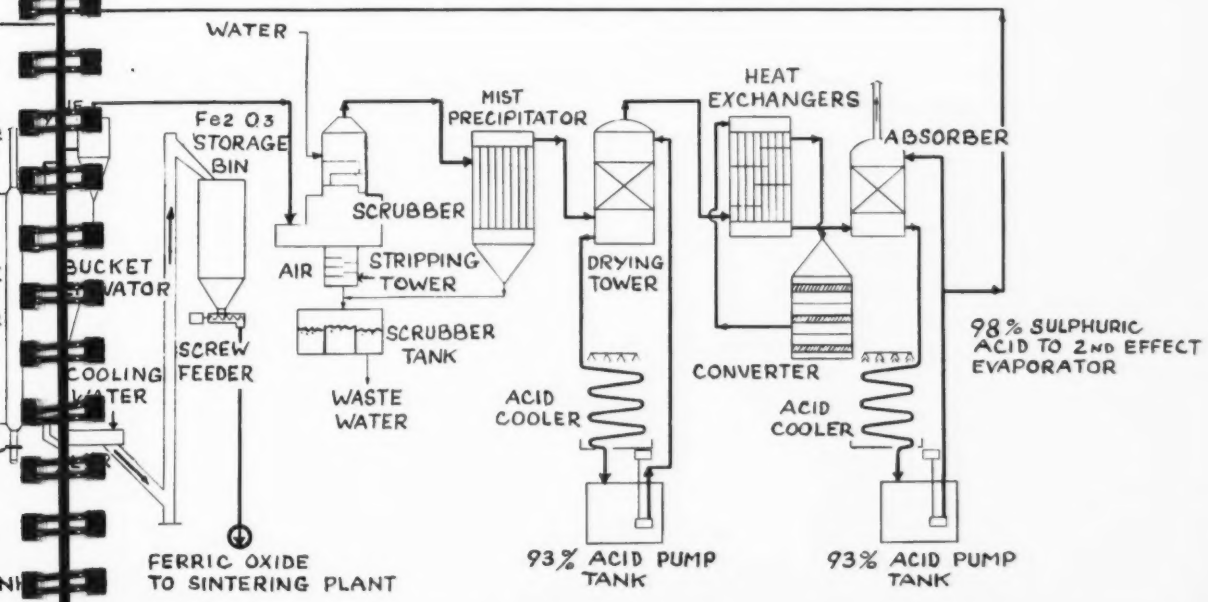
ACID REGENERATION.

Economics of the process are attractive in that regenerative cost of the acid is under $19.00/ton on a 100% basis, excluding iron oxide credit. Technological advantages are also claimed.

H_2SO_4 Regeneration

Spent pickle liquor from the pickling lines is collected in rubber-lined steel tanks. Spent acid is then pumped to the first effect of a double-effect vacuum evaporator crystallizer. This evaporator is constructed of a Karbate exchanger and rubber-lined steel body. Low pressure steam in the exchanger concentrates acid to a point just below saturation concentration of ferrous sulphate. Steam evaporated from the first effect is fed to the steam side of the heat exchanger of the second effect. The heat load is optimally balanced for the best economy.

Partially concentrated spent acid from the first effect and sulphuric acid produced in the contact plant are fed to the second-effect evaporator-crystallizer which is a forced circulation design of Nionel tubes and rubber-lined body. Ferrous sulphate is crystallized as monohydrate and the acid is concentrated to above 44%. Operating temperature of this evaporator-crystallizer is about 135°F, a barometric condenser and two-stage jet ejector being used. At this acid concentration and operating temperature, ferrous sulphate solubility is limited to about 3%. The heat of dilution of concentrated sulphuric acid and the sensible heat of liquor from the first effect are used advantageously in the second evaporator. As low operating temperatures are used for the evaporators, relatively inexpensive materials of construction —rubber-lined steel and Nionel—can be used, thus reducing capital costs. A rubber-lined settling tank operates in conjunction with the crystallizer to control the amount of solids in the evaporator body and the size of the crystals. The slurry containing about 30% solids is fed to a centrifuge. Washed cake from the centrifuge containing about 15 to 20% moisture is transferred from the wet cake feeder to the roaster.



FERROUS SULPHATE ROASTING. CONTACT SULPHURIC ACID PRODUCTION.

Singmaster and Breyer regeneration plant flow diagram

Roasting Ferrous Sulphate

Washed ferrous sulphate monohydrate cake is continuously fed to a rubber-covered belt conveyor and carried to the top of a multiple-hearth furnace. Coal fines and sulphur are added to the wet cake to ensure proper roasting conditions and sufficient sulphur-bearing gas to the acid plant to make the total pickling and regeneration plant self-sufficient with respect to sulphuric acid.

Filter cake is first dried by hot gases passing countercurrent to the cake. Decomposition of ferrous sulphate begins at 800°F and is complete at about 1,200°F on the bottom hearth, where iron oxide is discharged to a jacketed conveyor for cooling. Iron oxide produced in the roaster contains less than 1% total sulphur, which can be readily eliminated in the sintering operations.

Gas from the roaster has an analysis which permits it to be fed almost directly to the contact acid plant (1.25 grains SO_2 per cubic foot at 700°F). Sulphur trioxide content of the gas can be about 25 mg. per cubic foot at normal temperature and pressure.

Estimated Operating Costs

	$/Day	
Labour and Supervision		
One lead operator per shift @ 3.50/hr.	84.00	
Two assistant operators per shift @ 3.00/hr.	144.00	
Supervision	25.10	
		253.10
Utilities and Chemicals		
Steam 17,000 lb./hr. @ 0.60/M.lb.	245.00	
Electricity 215 k.W @ 0.01/k.W.h.	51.70	
Cooling water 2,400 g.p.m. @ 0.01/M.gall.	34.60	
Fuel gas 7.2 MM B.T.U./hr. @ 0.45/MM B.T.U.	77.80	
Coal fines 6,000 lb./day @ $4 ton	12.00	
Sulphur 2,160 lb./day @ $22/ton	23.80	
		444.90
Maintenance		302.00
Laboratory and Supplies		50.20
Payroll charges and direct overhead		131.40
General mill overhead		52.50
Fixed charges: depreciation, real estate taxes, insurance		362.40
TOTAL		**1,596.50**
Balances:		
Credit		
H_2SO_4—84.7 tons/day @ $22/ton		$1,863,40
Iron Oxide — 33.5 tons/day @ $10/ton		335.00
Operating Costs		$2,198,40
		$1,596,50
Profit before taxes and interest		$ 601.90

Contact Acid Plant

Hot gases from the cyclone dust collector pass to a contact sulphuric acid plant equipped with standard Peabody scrubber, mist precipitator, heat exchangers and converters. The gases are water quenched in the scrubber for water vapour and dust removal, then pass into the electrostatic mist precipitator for SO_3 and H_2O mist removal. They are then dried in a packed drying tower with sulphuric acid before passing through three heat exchangers. SO_2 with excess oxygen is converted in the converter to SO_3 and eventually absorbed by H_2SO_4 to make 98% acid.

Products	
H_2SO_4 (100%)	3.525 tons/hr.
Iron Oxide	1.395 tons/hr.

Estimated Utilities and Chemicals Requirements	
Steam (150 p.s.i.g.)	17,000 lb./hr.
Water (Cooling)	144,000 gallons/hr.
Fuel (Natural gas)	7.6 million B.T.U./hr.
Electricity	215 k.W.
Coal Fines	250 lb./hr.
Sulphur	90 lb./hr.

Recovery Process Economics

Sulphuric acid produced by the plant is stated to be equivalent to the sulphuric acid consumed by the pickling operation plus losses incurred during the pickling and regenerative steps.

The total capital investment required to treat 100,000 gallons (500 tons a day) of 8.5% H_2SO_4 and 13% $FeSO_4$ waste pickle liquor is estimated at $2,110,000.

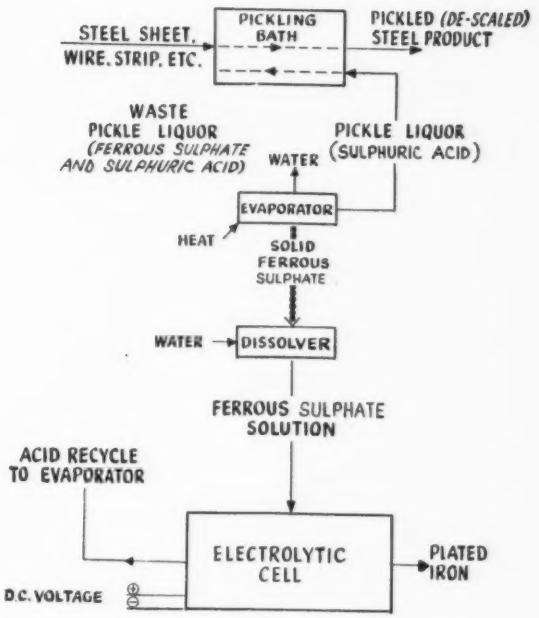
Estimates show that this integrated waste pickle liquor regenerating plant is not only self-supporting but would be attractive as an investment to the steel industry. Regenerative cost of sulphuric acid is under $19 a ton on a 100% basis (1959 prices), without taking into account credit for the recovered iron oxide and under $15 a ton of acid when a credit of $10 a ton of iron oxide (1959 prices) is allowed; no provision is made for interest on capital.

This compares with the spray-evaporator process (U.S. Patent 2,668,130) for which a conversion cost of $29 a ton for regenerated acid is reported while the sulphate-chloride Ruthner process (U.S. Patent 2,785,957) reports a conversion cost of $33.20.

Electrolytic Recovery of Acid and Iron from Waste Pickle Liquor

Ionics' Cation Exchange Membrane Process

Ionics process for recovery of sulphuric acid and iron from waste pickle liquor in the steel industry



AN electrolytic process using a cation exchange membrane which proposes to produce 95 tons a day of 25% acid (contaminated with 4.5% $FeSO_4$) equivalent to 85 tons a day iron-free or fresh acid, and 24 tons a day of iron plate, was described recently by Walter Juda, Thomas A. Kirham and Edgardo J. Parsi of Ionics Incorporated at the 15th Purdue Industrial Waste Conference. Investigations have been limited to the more difficult problem of recovering waste pickle liquor from continuous lines in large operations.

Ionics' Electrolytic Cell

The electrolytic ferrous sulphate conversion cell designed by Ionics Limited has three compartments—cathode department, defined by the iron cathode and a porous (asbestos) diaphragm, a centre compartment defined by a porous diaphragm and the cation exchange membrane, and a lead anode. Heptahydrate from the crystallizer, with some excess acid clinging to the crystals, is dissolved in water and the slightly acid ferrous sulphate solution is introduced as catholyte into the cell through the porous diaphragm and out of the centre compartment. Sulphuric acid is placed in the anode compartment. D.C. voltage is applied. Iron is plated at the cathode and oxygen gas is evolved at the anode with hydrogen ions transferred through the cation membrane into the solution in the centre compartment. Hydrogen ion efficiency of the cation membrane in this process is stated to be better than 90%. The membrane also serves to prevent any direct contact of iron with the anode. The flow of liquor through the porous diaphragm in the direction opposite to that of the hydrogen ions prevents the catholyte liquor from becoming too acidic, thereby maintaining the plating efficiency at about 90%. Half of the iron fed to the cell can be plated, the other half remaining in the cell liquor. This latter, which can be adjusted to have the same composition as the spent pickle liquor, is returned to the evaporator crystallizer.

Laboratory Cell Operation

The experimental cell operated by Ionics Limited utilized two lead anodes, each $\frac{1}{8}$in. thick, two 9in. by 10in. nepton CR-61 cation membranes, two $\frac{1}{32}$in. porous diaphragms made of asbestos and a central double iron cathode. Iron was plated on both sides of the central cathode.

The following spacings were used:—

Anode to cation membrane	$\frac{1}{4}$in.
Cation membrane to diaphragm	$\frac{1}{4}$in.
Diaphragm to cathode	1 in.
Anode to cathode	1—1$\frac{1}{2}$in.

A 30% solution of ferrous sulphate made from heptahydrate crystals was fed to the cell and the temperature maintained at about 80 to 90°C. The flow rate of cell liquor was 8.5 c.c./

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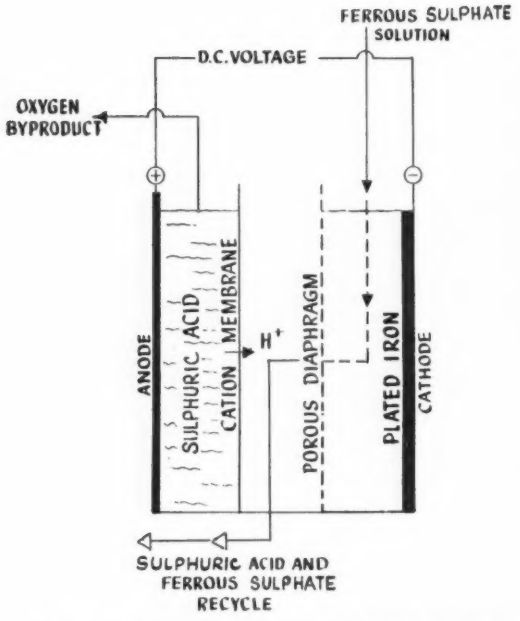
← Underground drilling of massive pyrites at Tharsis. These stopes are 100 ft wide by 600 to 1000 ft long.

...Europe's principal source of sulphur



Electric membrane cell for recovery of iron and acid

min. Voltage was 4.2 and runs were carried out for periods up to four days.

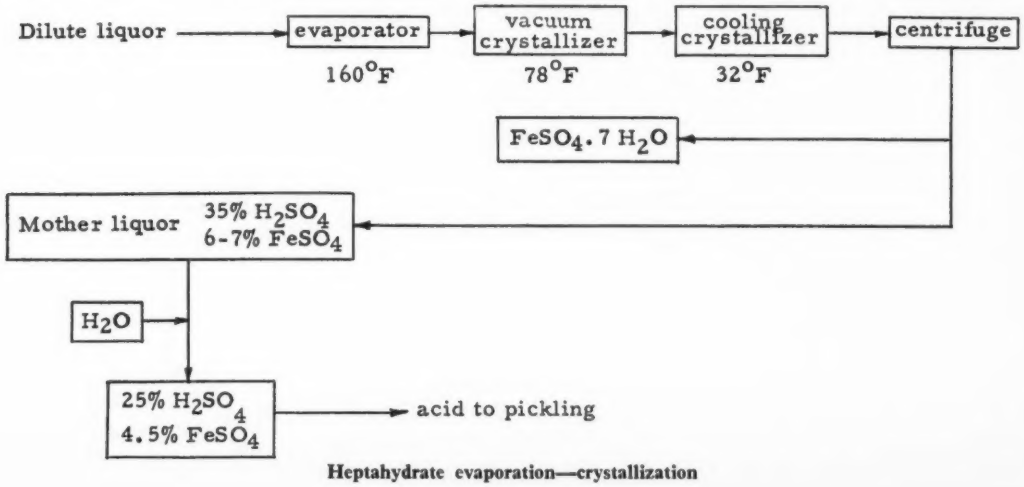
Evaporation and Crystallization of $FeSO_4$

Several processes have been worked out using either ferrous sulphate monohydrate or ferrous sulphate heptahydrate. The monohydrate processes have the advantage of producing more easily a concentrated liquor containing a minimum of dissolved residual ferrous sulphate. They are more costly, however, compared to heptahydrate crystallization. Where ferrous sulphate is either discarded or roasted, the monohydrate has the advantage of lesser weight or lower water content than the heptahydrate. In the Ionics' process, use of the heptahydrate requires less water addition to the dissolver or less additional evaporation. Also, the heptahydrate crystals are found to retain less sulphuric acid, so being preferable as a suitable cell feed.

Prior to use in the Ionics' cell, waste pickle liquor is evaporated at 160°F and ferrous sulphate is then crystallized in a vacuum crystallizer, cooled down to 30°F. Crystals are separated from the mother liquor by centrifugation. The mother liquor is diluted to 25% acid, so reducing the residual ferrous sulphate to 4.5% and the solution is returned to pickling.

Economic Analysis

Different recovery processes are being evaluated by the "Orsanco" Committee on a standard basis (Table 1) — namely cost of recovery acid from 100,000 gallons per day (g.p.d.) of waste pickle liquor containing 8.5% of sulphuric acid and 13% of $FeSO_4$. In evaporation, the acid concentration of the mother liquor and its residual $FeSO_4$ content



Heptahydrate evaporation—crystallization

Table 1

Orsanco Basis

Volume of Spent Liquor ...	100,000 gal./day
Weight of Spent Liquor ...	500 tons/day
Composition	13% $FeSO_4$—8.5% H_2SO_4
Total Acid	85 tons/day
Bound Acid — 42.5 tons/day	
Free Acid — 42.5 tons/day	
Iron	24 tons/day

Table 2

Typical Operating Data

Current density (amp/ft²)	50
Voltage	4.2
Influent composition	5.4 (30%)
eq./litre $FeSO_4$)	(pH 1.1)
Effluents composition eq/litre	
$FeSO_4$	2.9 (16.5%)
H_2SO_4	2.8 (10.4%)
Plating efficiency	90%
% Conversion	50%
K.W. hr./ton iron	4,450

Table 3

Orsanco vs. Ionics' Recycle

	Orsanco (100,000 g.p.d.)	Ionics' Recycle
Spent Liquor	500 tons/day	500 tons/day
H_2SO_4	8.5%	10.4%
$FeSO_4$	13%	16.5%
Dilute Cell Liquor ...	None	410 tons/day
H_2SO_4	—	10.4%
$FeSO_4$	—	16.5%
Total to Evaporation ...	500 tons/day	910 tons/day
Products of Evaporation		
Water evaporated ... (to 35%)	270 tons/day	400 tons/day
Evaporated Liquor ...	124 tons/day (35% H_2SO_4-7% $FeSO_4$)	270 tons/day (35% H_2SO_4-7% $FeSO_4$)
H_2SO_4 (100%) ...	43 tons/day	95 tons/day
$FeSO_4.7H_2O$	106 tons/day	240 tons/day

is important as residual ferrous sulphate recycled in pickling increase the daily acid requirement due to its effect on pickling rates. While the acid strength is above 20% there is little effect on pickling rates up to impurity levels of about 5% $FeSO_4$.

Material balance shows that 95 tons a day of 25% acid containing 4.5% $FeSO_4$ are required for descaling 85 tons a day of iron free acid. The 85 tons a day figure corresponds to the total sulphate content of Orsanco's 100,000 g.p.d. basis. To limit the extra acid to 95 tons a day, without slowdown in pickling, acid concentration should not drop to as low as 8.5%

Comparing a hypothetical Orsanco basis heptahydrate evaporation process with Ionics' complete recycle (Table 3) it is noted that evaporation under the Orsanco heading produces only 43 tons a day of regenerated acid from the 8.5% pickle liquor, i.e. nearly one-half the acid requirement, whereas Ionics' recycle recovers the entire acid content. It also requires very much less than double the evaporation because of the higher acid concentration of the spent liquor and the high water content of the heptahydrate.

The material balances show, in fact, that to accomplish Orsanco's 100,000 g.p.d. recovery target, Ionics' process proposes to produce 95 tons a day of 25% acid (contaminated with 4.5% $FeSO_4$) equivalent to 85 tons a day of iron-free or fresh acid, and 24 tons a day of iron plate.

Economics of the process are summarised in Table 4. Uncertainties indicated by the range of cost figures, Ionics say, reflect the absence of pilot plant operation. Uncertainties in the credit ranges are due to local variations in the value of scrap iron and pig iron, sulphuric acid and disposal costs. Nevertheless, it can be seen that the process is profitable; the iron value is, however, essential to render the process profitable.

Continuous vs. Batch Pickling

The above has dealt with recovery of waste pickle liquor from continuous lines in large operations, but there are, of course, small operations carried out requiring three to five tons a day of acid. In batch liquor, the small amount of free acid makes it possible to eliminate the evaporation-crystallization step. Ionics are at present investigating the direct plating operations and cost of batch pickle liquor.

Table 4

Economics of Ionics' Process

(of 95 tons/day iron contaminated acid, equivalent to 85 tons/day fresh acid and 100,000 gal./day spent liquor)

Operating Costs $/ton acid (fresh basis)	
Electricity @ 0.9 cents/kW hr. (D.C. and refrigeration)	$10.00—12.00
Steam @ 0.60 cents/1000lb.	4.00 5.00
Cooling water @ 0.10 cents/1000gal.	0.10
Labour @ 3.00/man hour	1.70— 3.40
Supervision—15% of labour	0.30— 0.60
Labour and supervision overhead—50% of labour and supervision ...	1.00— 2.00
Depreciation, 6% of investment ...	3.00— 4.00
Maintenance, 3% of investment ...	1.50— 2.00
Supplies and laboratory, 1% of investment	0.50— 0.70
Anode and membrane replacement ...	1.30
Steel cathodes	2.00
Total Cost	**$25.40—33.10**
Credit $/ton acid (fresh basis)	
Iron @ $35/ton—$70/ton	$10.00—20.00
Sulphuric acid @ $20/ton—$24/ton	20.00—24.00
Disposal or neutralisation cost ...	7.00—25.00
Total Credit	**$37.00—69.00**

Recycling Usable Acid with a Novel Mercury Cell

New Siemens and Halske Process

An addition to the range of new processes for treating waste acid from pickle liquor is that developed by Siemens and Halske of Austria. A mercury cell is used.

Siemens and Halske's process, proved in pilot-plants at Brevillier and Co., Vienna and A. Urban and Sons, Neunkirchen, separates iron as a mercury amalgam in the primary cell where acid is regenerated. The iron is then plated out in a secondary circuit at a carefully controlled pH.

In the new process segregation of the iron is the first step. The spent pickling acid is pumped through a special acid pump to the primary cell, a mercury cathode unit. Mercury flows through the bottom of the cell which is tilted at an angle of 1°. The anodes in the top of the chamber are made of Pb-Ag alloy. Anodes are separated from passing pickle liquor by porous diaphragms to permit migration of $SO_4 2-$ ions to the anode chamber.

For the anode reaction, water is added:

$$2SO_4 2- + 2H_2O = 2H_2SO_4 + O_2 + 4e$$

Cathode reaction is the reduction of iron which forms an amalgam with the mercury:

$$Fe++ + 2e = Fe$$

About 4gpl of iron is removed per pass.

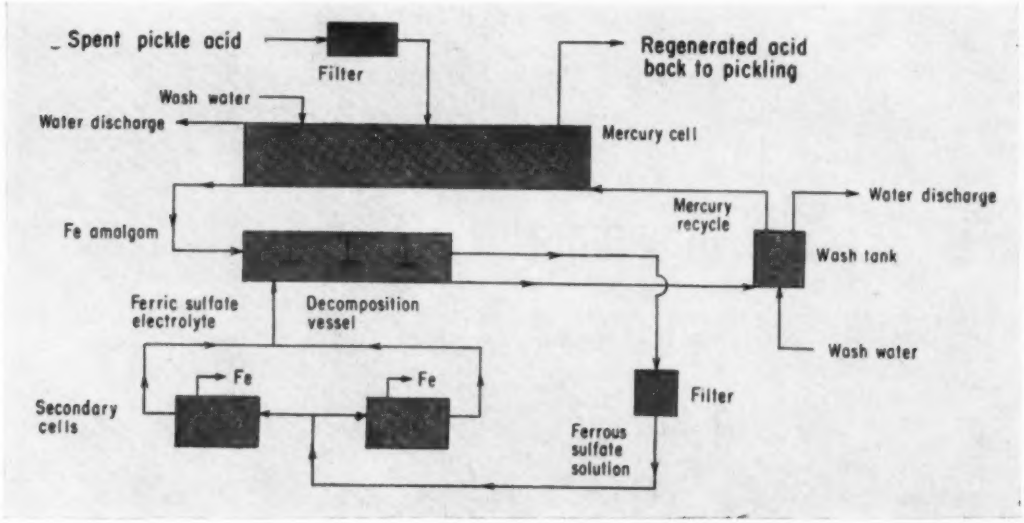
Treatment of Amalgam

From the anode chamber regenerated acid combines with $FeSO_4^-$ depleted pickling acid (washed off the surface of the amalgam), and is returned to the pickling line.

From the primary cell the mercury — iron amalgam passes to a separation vessel for mixing with ferric sulphate electrolyte from the secondary cells. Iron goes back into solution freeing mercury which is recycled to the primary cell after washing:

$$2Fe+++ + Fe = 3Fe++$$

Ferrous sulphate solution flows to the secondary cells constructed in filter - press



Flow diagram of the Siemens and Halske process

fashion. At the steel cathode iron plates out and at the lead anode ferrous iron is oxidized to ferric, the cell pH being about 1.5.

Advantages Claimed

The high operating temperature of 140° to 212°F eliminates the need to cool incoming pickling acid. Regenerated acid, however, returns to the process at a usable temperature.

The process also provides the ability to hold the Fe content of the pickling bath at a low, preset value. About 25 gpl Fe appears in acid returned to the process. The low constant Fe concentration enables pickling line production to be increased, Siemens and Halske claim.

Operating Data

Some operating data have been obtained, based on pilot plant investigations, for a unit to regenerate 95 tonnes a month of 100% sulphuric acid. Included in operating costs are 720kW of cell power, 25kW for pumps and other equipment, 560 man-hours of labour, 6 tonnes of steam, 70,620 cu. ft. of water and about 38 man-hours maintenance. Based on Austrian costs this totals £1,900 approximately.

On the credit side, some 95 tonnes of sulphuric acid are recovered and 51 tonnes of iron, as well as a saving of 100,000 K cal. a month in the heat balance of the pickling operation. Again based on Austrian costs, and excluding amortization of the plant's capital costs and savings in conventional disposal costs, this works out at a total cost of £1,970 approximately.

Ceramic Filter for Removing Acid Mist from Exit Gases

In recent years demands to reduce air pollution caused by exit gases of chemical plants have been raised in various quarters. The chemical industry has thus found it necessary to consider purifying exit gases even if these are within the requirements laid down by H.M. Alkali Inspector. Sulphuric acid mist in the exit gases of some sulphuric acid plants has been found particularly troublesome even when present only in very small quantities. Acid mists amounting to as little as one-half to three-quarter grains/ft^3 (1.72 grammes/m^3) expressed as SO_3 have caused complaints owing to the tendency of the mist to "fall down" and thus to affect the neighbourhood of the plant. Some years ago Lurgi G.m.b.H., Frankfurt/am Main, developed a process for the removal of the acid mists from exit gases which has proved efficient and inexpensive. This process, which is patented in the U.K. and many other countries, has been licensed to Huntington, Heberlein and Company Limited, London, for exploitation in the U.K. and the British Commonwealth.

The Lurgi process, which is known as the "Ceramic Filter" process, utilises for removal of acid mist a porous layer made up of granular material, the particle size of which is generally of the order of 0.5 to 3 mm. The thickness of the filter material may vary between 5 and 30 mm.

Efficiency of the removal of mist droplets in the filter material is a function of the gas velocity. Coarse mist particles coagulate in the filter material at lower velocities than finer mists. One can thus say that the efficiency of the filter is a function of the mist particle diameter and that fine mist particles necessitate a larger pressure drop than coarse particles.

In a ceramic filter designed for the removal of sulphuric acid mist from the exit gases, ceramic filter tubes or "candles" are generally used, through which the mist containing gases pass from the inside to the outside. With this arrangement similar efficiencies can be obtained with a lower pressure loss than when working from the outside to the inside. The mist particles which coagulate in the filter material form larger droplets which run down the outside of the filter tube in the form of liquid sulphuric acid.

A number of ceramic filters have been installed which precipitate 78% sulphuric acid with an efficiency of approximately 99.9% at pressure losses of the order of 12in. When removing mist used in wet contact plants, mist quantities up to 100 grammes H_2SO_4/m^3 have been successfully removed. A typical example of the acid composition was:—

Size in Microns	Relative No. of Particles
0-1	12%
1-2	54%
2-3	27%
3-4	7%

In a similar way, mist from the exit gases of the Kachkaroff type sulphuric acid plant at the Phoenix Wharf Chemical Works of the South Eastern Gas Board, which has a rated daily capacity of 50 tons of sulphuric acid (100% H_2SO_4), has been removed with efficiencies of about 98% to 99% at pressure differences as low as 6in. to 8in. In a three-monthly test carried out last year the average inlet burden in the form of acid amounted to 0.615 grains SO_3/ft^3. After having passed through the ceramic filter the gases contained only on the average 0.009 grains SO_3/ft^3.

Kachkaroff plant at SEGB's Phoenix Wharf Works with the two stacks and in the bottom right corner the housing for the ceramic filter

Formerly, sulphuric acid mist could be seen descending slowly over a wide area. Since the ceramic filter has been in operation, acid fumes are no longer visible and only occasionally are small amounts of nitrogen oxides noticed.

Exit gases of SEGB's Phoenix Wharf acid plant are drawn by a fan through the ceramic filter from the base of the stack through which they previously passed to atmosphere. In the filter the mist-containing gases pass through tubes made of a ceramic material of controlled porosity from the inside to the outside; the mist particles coagulate and liquid acid runs down the outside of the filter tubes. The acid thus obtained is collected from the base of the filter and returned to the Kachkaroff plant.

Troublesome Solid Impurities

Solid impurities in the gases are, of course, somewhat troublesome since they may choke the filter material. At the above mentioned Kachkaroff plant a certain amount of solids is entrained in the gases entering the filter, but it has been found possible to clean the filter material comparatively quickly and easily so that the candles can be used again. Under conditions such as above it may be desirable to install a ceramic filter unit designed for a larger gas volume and to recirculate part of the gases.

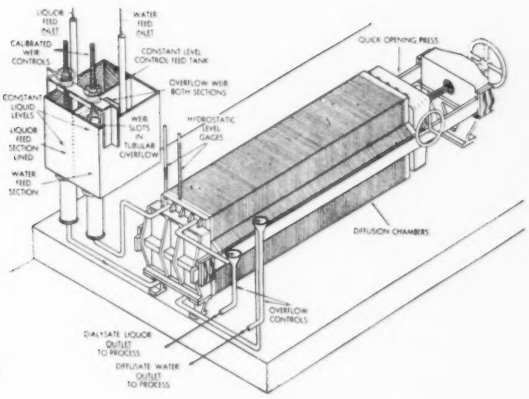
As already indicated, the efficiency of the ceramic filter depends to some extent on the mist particle size. In anhydrite-cement contact sulphuric acid plants the acid mist is generally extremely fine and unless the gases are well humidified very high gas velocities are required or the efficiency is low.

Tests are being carried out in connection with the exit mist leaving contact sulphuric acid plants in which sulphur or acid sludge is used as raw material. The indications are that these mists—without humidifying the gas—can be removed efficiently at relatively low pressure differences. Under certain conditions it may be preferable, however, to humidify the gases so as to reduce pressure losses at the same efficiency.

Ceramic filters, while developed for removing sulphuric acid mist, are expected to be suitable for other gases and mists but the process is so new that no generalisation can as yet be made.

Dialysis for Acid Recovery

Using the Graver Hi-Sep Process



Dialysis system showing all components and indicating flow pattern

DEVELOPMENT of acid-resistant plastics has opened up new fields of application for the 100-year-old unit operation of dialysis. This process, long limited to laboratories and one or two industrial applications, can now be used on a much wider scale for the separation, recovery and purification of acid liquors.

Although to date dialysis has not found application in pickle liquor separation, its merits point to its use on small pickle lines where low-cost acid recovery is of greater significance than utilization of copperas.

Operation

Dialysis is a simple and inexpensive method of separating constituents of a liquor by passing them through a membrane. No power is required and no chemical agents are involved with the result that operating costs are extremely low.

Construction and material of membrane are important, since high diffusion capacity as well as toughness and durability are required. Each solute has its own rate and transfer coefficient in a given dialysis set up. Good performances means extracting a suitable amount of the wanted solute and as little as possible of other compound. A weak but fairly pure solution of the desired solute is obtained.

Dialyzers hold the permeable or semi-permeable membrane in place and contain and properly distribute the counter flowing solutions. Characteristics of the membrane determine dialyzer design and three distinct types are recognized :

- The Cerini dialyzer in which impregnated membrane bags are suspended in a tank of liquor, liquor to be recovered passing on the inside of the bags.
- A tank-type in which membrane tubes are supported vertically in the tank.
- A filter-press type in which membranes are held between alternate liquor and solvent frames in a plate-and-frame arrangement.

Among present-day filter-press dailyzers are the Dutch Kooij dialyzer and in the United States the Graver "Hi-Sep" dialyzer. This latter is used in acid-recovery operations and apart from permitting the re-use of acid, enables other valuable products in a liquor to be recovered by removing acids.

Large Tonnage Acid Recovery

Designed to provide maximum recovery and trouble-free, economical operation with the lowest possible requirements on space, maintenance and operator time and attention is the Graver Hi-Sep dialyzer. At rates of 50-500 gallons per hour and more, depending on the size of the unit, the Hi-Sep dialyzer can recover several hundred pounds and up to one-half ton of product per hour. This is possible by virtue of :

- Membranes with very high mass transfer capacity.
- Air-free operation with no bubbles to impede smooth and efficient flow through the unit.

- High acid-resistance of the membrane which allows use of high concentrations of acids resulting in more rapid diffusion.
- Cross and counter flow movement of liquids to assure most complete separation.
- Thinness of the membranes and frames which makes possible the use of 2,000 sq. ft. and more of effective membrane area per unit.
- No power requirements except for pumps.

Design of the Dialysis System

The Graver Hi-Sep dialysis system consists of a feed arrangement, receiving tanks and a plant-and-frame structure to hold the membranes. As the plastic membrane employed is extremely thin (it is believed to be the thinnest ever developed) a light structural support only is required. The membranes are composed of durable vinyl polymers of 0.0042in. thickness and have a uniform and controlled porosity.

The dialysis portion of the system is composed of alternate liquor and water cells formed by the frames and membranes, both of which have ports. The frames rest on two horizontal bars of the unit. To form the water-tight compartments, the unit has head and tail stocks which when brought together under pressure by a hand-operated screw hold the frames in a vice-like grip. Between the membranes are unique chemically-resistant spiral separators which maintain the effective operating area in each cell. All supporting members and tanks are of metal—steel, stainless steel or cast iron. The feed tank is lined for protection against acid corrosion. Piping for the liquor flow is also corrosion resistant.

Operation

No power is required since the dialysis process is activated entirely by the concentration gradient between the liquor and water cells. The only power needed is for pumping the liquor and water into the feed tank and back to process or storage.

Water and liquor enter separate inlets in the feed tanks. Inlet pipes are below the liquid levels and are designed to eliminate formation of air bubbles. Feed rates are controlled by tubular overflows with weir slots. Flow of water and liquor are individually regulated and once set constant feed rate is assured by the continuous overflow of both liquids over the overflow weir which keeps a constant level on the weir slot. Overflow is returned to the incoming feed system.

From the feed tank, the process liquors enter the dialysis portion of the system, flowing along conduits formed by the joined parts of the membranes and frames. Liquor travels along the bottom and water through the top. Liquor entering each cell passes upward and across the membrane, leaving at the top. Water takes the opposite course, passing downward, across and out at the bottom. The cross and counter flow assures the greatest separation by providing the longest possible hold-up time and the highest acid concentration differences at every point across the membrane when diffusion takes place. Both liquids—the liquor (dialysate) and the water (diffusate) flow out of the unit continuously and are collected in separate receiving tanks. Automatic shut-off is provided should either feed be interrupted.

Applications

Use of the Graver dialysis unit is not restricted to any special group of industries. It has proved valuable, however, in any field where acid, alkali or waste-liquors can be profitably separated for the purpose of product recovery, purification and re-use. There are many acid-recovery operations for which this dialyzer can be used: thus it can recover acid in ore processing; in the plating room for recovery of contaminated plating solutions by removing the metallic cations from the solution and replacing them with hydrogen ions; and in pickling operations.

The acid-resistant membranes have more than twice the mass transfer capacity of parchmentized paper—a coefficient of 2.40 as compared with 1.05. Hence they are capable of very high separation and recovery. Depending upon the concentration and rate of flow on the liquor side, recovery of up to 90% can be achieved, with the acids ending up as a 10-60% solution. On a per-hour basis, this can result in several hundred pounds (weight) and up to a half-ton of recovered product.

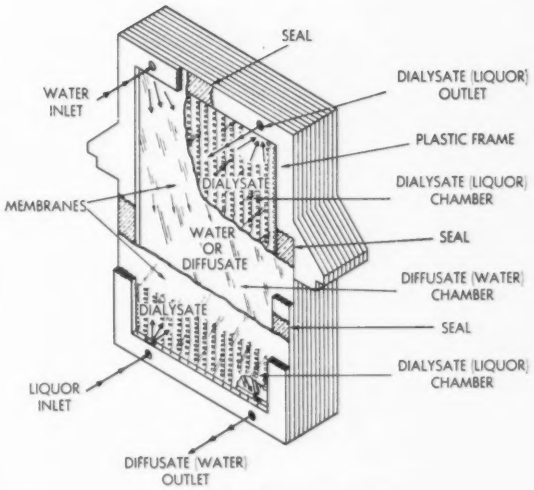
For example, 500 g./l. of sulphuric acid in the liquor side will result in 450 g./l. in the water side, producing a 35.5% solution. Acid concentration in the liquor can be as high as 700 g./l. (50%), in which case there would be a recovery of 350-360 g./l. for a 29-46.5% solution. In general, the lower the operating rate the higher the recovery because more hold-up time is allowed.

In acid recovery of contaminated plating solutions dialysis removes the acid and returns recovered acid to the bath at concentrations varying from 60 to 90% of the concentration of the contaminated waste solutions.

Advantages and Limitations

Compared with previous dialysis equipment, the Graver dialyzer can cope with two or three times the work at a fraction of the capital investment. It has a low power requirement (for transfer pumps only) and therefore has a surprisingly low operating cost—it makes possible important production savings through the re-use of acids and the recovery of other products. Another advantage is the reduction of neutralization requirements.

Probably the most important operating feature of the method is the high-rate transfer, due to the properties of the membrane and design features of the system. Maintenance is low as the membranes will operate for many years, being sturdy and having a high tensile strength. The equipment requires at the most the part-time services of a single operator to check and see that the feed and recirculating pumps are functioning properly. Low space



Dialysis chambers or "cells"

requirements and ability to operate on tap-water are other noteworthy considerations.

A basic limitation on operation is the need for sufficient concentration gradient in the liquor to supply the driving force necessary for diffusion. Also, temperatures above 120°F in liquors may have a deleterious effect on the plastic membranes although high-temperatures can be countered in the dialysis unit by cooling from water cells. Process liquors, too, should be preferably clear with a minimum of sludge content, since the presence of heavy sludge can reduce efficiency of the pipes and result in increased maintenance. This is overcome, however, by the design of the dialyzer unit, whereby the residue sludge can be flushed out.

Phelps-Dodge Process for Dialytic Acid Recovery

WITH a background of pilot-plant experience gained in 1947-48, Phelps-Dodge Refining Corporation have installed dialyzer capacity at their El Paso Refinery. The company started using dialysis in their nickel sulphate plant in 1957, and afterwards recovered H_2SO_4 from some process streams at their Laurel Hill, New York, works.

Pilot-plant Experiences

In their pilot-plant dialyzer Phelps-Dodge treated a $NiSO_4$-H_2SO_4 electrolyte stream of refinery series-system liquor. The solvent was water as was the case in all subsequent work. The membrane used in early work was 850sq. ft. of parchmentized kraft paper. Sulphuric acid was extracted satisfactorily but the opera-

	$NiSO_4$ Plant			$CuSO_4$ Plant (Nalfilm D30)	
Dialyzer Feed liquor	**Parchment 1957**	**Nalfilm 4 1957-1958**	**Nalfilm D30 1958**	**With preconcentration**	**Without preconcentration**
g.p.m.	3.11	2.94	2.36	7.24	7.30
gr./l. free acid	240.60	290.50	295.90	294.90	247.50
Acid transfer rate lb./hr.-sq. ft. ...	0.113	0.151	0.304	0.275	0.169
Acid transfer co-efficient lb./hr.-sq. ft. (gr./cc.)	0.801	0.858	1.47	1.744	1.072
Acid Product stream (diffusate)					
g.p.m.	2.64	2.86	1.87	7.08	7.15
gr./l. free acid	73.10	89.40	82.30	112.10	76.60

tion was not considered practical because the membrane required frequent replacement. In 1956, the company decided to try dialysis again, this time in the $NiSO_4$ plant. The same dialyzer, with parchment membrane, was used. The feed liquor contained $NiSO_4$ and H_2SO_4 and also some significant amounts of impurities, mainly sulphates of iron, arsenic and Sb. The unit operated for six months, actively on stream for about 60% of the time. Forty-five membrane changes, however, were needed in the period.

Choice of Membrane

Vinyl membrane materials which showed promise were investigated about 1956, and one, Nalfilm 4, lasted for three months and acid transfer coefficient was good. After about a year, a new vinyl material was developed, Nalfilm D30, with no fixed ionic group, which was found to have a much higher acid transfer coefficient. It was also decided to change to a smaller dialyzer with about one-third as much membrane surface and this change gave increased acid transfer.

Phelps-Dodge extended dialysis to their $CuSO_4$ plant to purify tank room discard liquor in 1958. Two new units with 1,700 sq. ft. combined membrane surface were bought. Feed-liquor was preconcentrated by evaporation with a high acid-transfer coefficient again being observed, but it was decided to operate in the $CuSO_4$ plant with preconcentration. This meant some sacrifice in capacity; it added process simplicity and avoided use of evaporator maintenance.

Performance Data

In the accompanying table, performance data are given for the Phelps-Dodge installations, which show the improvements in acid transfer coefficients with the changes in membrane materials. The process has proved to be a simple way to extract acid from process liquors with the minimum of operating labour.

Oleum Outlet Valve Emergency Repair

WHEN a bottom outlet gate-valve in a 500-gallon batch tank containing 20% oleum became stuck in the closed position, the problem was solved despite snapping off one of the hooks engaging the rising stem when attempting to open the valve.

Faced with the problem of replacing the valve without the necessity of emptying the tank, a simple solution was found by driving a conical lead plug into the open outlet pipe in the tank bottom. This plug was rigidly attached to one end of a piece of 1-inch pipe. Since there was little head-room over the tank, the pipe had to be made up of several shorter pieces poined together, as the pipe was lowered by means of couplings.

Recovery Process for Sludge Acid

With Particular Reference to the Miley and Chemico Processes

THERE are three types of sludge acid recovery plants in use:—

- Hydrolysis and concentration
- Complete combustion
- Thermosplitting

Hydrolysis of acid sludge, that is separation of the oily or hydrocarbon part by addition of water and steam has been used in the past, and the weak acid obtained subsequently concentrated. Today few—if any—plants of this type are being built, since they are too costly to maintain and operate, and the product acid obtained is so weak that it must be fortified with strong oleum before it is suitable for use in treating oil. Complete combustion of the sludge and thermosplitting of the sludge are considered to be the only profitable methods which are being used at present.

Complete Combustion

Most suitable for the complete combustion recovery process are sludges high in acid strength and low in hydrocarbon content. Therefore it is most suitable for alkylation sludges which contain about 90-92% H_2SO_4, 6-8% hydrocarbons, and 4-5% H_2O. Sludge or blends of alkylation and low acid content sludge containing as little as 65% H_2SO_4 and up to 25% hydrocarbons have been used recently on a profitable basis.

The complete combustion process consists of spray burning the spent acid in a large furnace equipped with oil or gas burners to supply the additional heat needed to split the H_2SO_4 into SO_2, O_2 and water vapour. The furnace is operated between 1700°F and 2000°F. Following the combustion furnace a waste heat boiler is used to produce steam and reduce the gas temperature to 700°F before it enters water coolers where it is scrubbed and cooled to 100°F. After cooling, the gas then passes through an electrical precipitator where acid mist is removed. The gas is then dried and oxygen content adjusted to the suitable $SO_2 : O_2$ ratio of at least 1 part SO_2 to 1.2 O_2 by volume. Conversion to SO_3 is effected in a conventional contact sulphuric acid plant equipped with heat exchangers of correct size that makes use of the outgoing hot convertor gases to heat the incoming SO_2 gases from 100°F to around 800°F.

When feeding straight alkylation sludges the resultant SO_2 gas after oxygen adjustment averages around 8% by volume. Sludge of low acid content and high hydrocarbon content will produce a gas lower in SO_2 percentage unless it can be fortified by burning sulphur or hydrogen sulphide.

It is claimed that if it is to be economically profitable to operate a contact plant on 5% SO_2 gas the equipment must be considerably larger and hence the investment greater than one built to operate on an 8% SO_2 gas. Such plants have a weak acid discharge from the water scrubber and precipitator that is usually neutralized with lime before discharge into streams.

The plant described above is similar to the one built by Chemical Construction for the Dixon Chemical Company of New York and described in detail on Page 32 of this issue. The same type of spray burning plant has also been built by the Monsanto Chemical Company.

Thermosplitting Method

Acid sludge that contains sufficient hydrocarbons will, when heated to 400°-500°F, be reduced by hydrogen evolved from the hydrocarbon into SO_2, H_2O, oil vapours and carbon. This method is therefore most suitable for sludge containing 35 to 70% H_2SO_4 and 50 to 20% carbon.

The carbon is removed from the system as a solid and the condensable oil and water are also removed before entering a combustion furnace where the non-condensable hydrocarbon vapours are burned to CO_2. Consequently the remaining SO_2 is quite concentrated, even when feeding sludges of low acid content and the gas, after oxygen adjustment

and ready for the convertor, will contain from 8 to 10% SO_2 by volume.

The combustion furnace and wet purification system are the same as used and described for the complete combustion method. The retort used in the thermosplitting process will cost more than a sludge burner but due to the highly concentrated SO_2 gas the contact plant will not cost as much as one designed to burn high carbon content sludges. Oil recovered from the gas stream is usually sufficient to supply the necessary heat. Carbon or coke obtained from the thermosplitting process is a valuable raw material and can be used in manufacturing activated carbon or carbon disulphide.

Types of Thermosplitting Process

In the United States, where there is considerable experience in decomposing acid sludge by heat, the processes have one feature in common, namely—heating a large volume of coke while in circulation and spraying the acid sludge on the moving coke stream. The only differences arise in the apparatus or method of carrying out the coke circulation, heating and mixing of sludge and coke.

The Chemical Construction Corporation (Chemico) process uses two kilns, one for coke heating and one for sludge and coke mixing, whereas Monsanto Chemical Company have used a muffle type of retort and heated the coke-sludge mixture through the brick. Sludge was sprayed on the moving bed of coke in the retort. G. Hunter Miley, who participated in the development of the first commercial acid sludge recovery plant which was built for Daugherty Refinery Division, Sonneborn Chemical and Refining Corporation, Pennsylvania, reports that his company uses a heat-exchanger for heating the coke through special stainless steel tubes and decomposes the sludge by spraying on the hot coke in a special type of conveyor mixer. There are now five installations of this type in the U.S.A. and one in Hamburg, Germany, and a further one is under construction in Hamburg and will be in operation shortly.

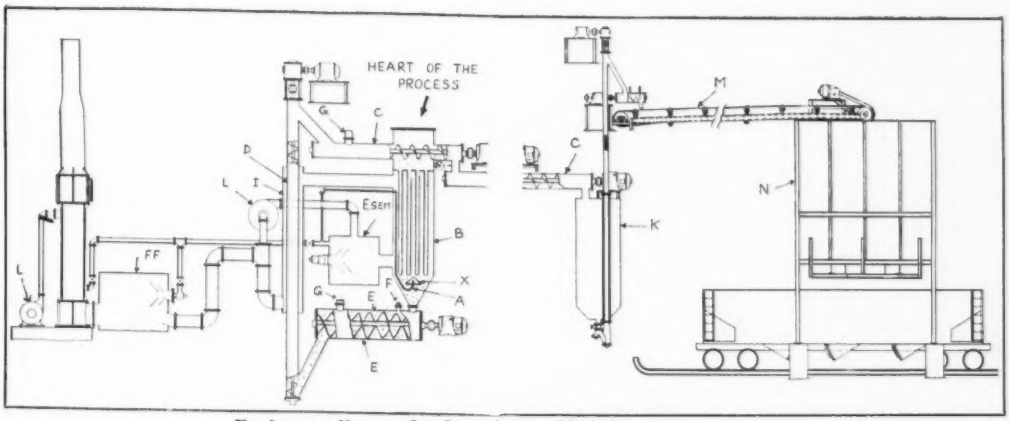
With the increasing number of alkylation units being installed throughout the world, the volume of acid sludges for disposals poses problems. In the U.S.A., and now increasingly in Europe, oil refineries and a nearby sulphuric acid manufacturer co-operate; the former provides a steady output for concentrated virgin acid and the latter while helping to solve the oil refineries sludge disposal problem obtains a low-cost source of sulphur.

The difficulties arising in disposal of sulphuric acid sludge has in fact caused a number of oil refiners to adopt hydrofluoric acid as a means of alkylation. There is little doubt, however, that the combination of oil refiner and sulphuric acid producer offers a more favourable economic solution to this problem. The processes and plants outlined below have proved their technical and economical merits and can therefore be expected to be used more widely still throughout the world.

Treating Acid Sludge by the Miley Process

DECOMPOSITION of sulphuric acid sludge to high purity SO_2 and coke is effected by the Miley process developed at Daugherty Refinery Division of Sonneborn Chemical and Refining Corporation, Petrolia, Pennsylvania, by G. Hunter Miley. Feature of the process, which employs a continuous cycle, is a specially designed retort into which the sludge is fed.

One type of feed for the Sonneborn plant is acid sludge obtained from white oil refining. Such sludge can vary widely in composition, titratable acid varying from 30% to 90% H_2SO_4. However, any acid sludge can be converted using the Miley process as long as it is pumpable and cokeable. The pumpability requirement is necessary in order for the sludge to be delivered to the plant in the correct form and the sludge must be cokeable in order to produce the discrete hard coke particles on which the functioning of the process depends.



Equipment diagram for Sonneborn acid sludge recovery process

The Retort

As mentioned above, the special feature of the plant is the unique retort into which the sludge is fed. The retort produces SO_2 and coke as its main products. A variable quantity of hydrocarbon vapours is also produced and these vapours are profitably used as part of the fuel required by the retort.

Two outlets for SO_2 are provided in the retort. By far the larger quantity comes from the lower outlet near where the sludge and coke first meet. A much smaller quantity of SO_2 is taken from the upper outlet. The SO_2 content of the gas from the outlets contains a higher percentage of SO_2 than a gas obtained from a sulphur burner, as when sulphur is burned the air required for combustion contains 79% of nitrogen which contaminates the SO_2 produced. In the retort, SO_2 is obtained from the sludge by decomposition without addition of any air.

Gas from the retort, however, contains some hydrocarbons which must be burned out before its SO_2 content can be converted to SO_3. This purification is carried out in a furnace, with addition of natural gas followed by water-scrubbing, Cottrell precipitation and oxygen adjustment. The retort gas is then comparable to gas derived from sulphur burning.

The other valuable product derived from the retort is coke, which is low in ash, low in acid content and relatively large in particle size.

Process Working

Sludge is admitted to the furnace by a conveyor-mixer (E), where it comes in contact with coke particles which are at a temperature between 450° and 650°F. The sludge is mixed with the hot coke and immediately begins to decompose; gas evolved flows through outlets (G). The coke produced mixes with the circulating coke and proceeds on its path through the retort.

The movement of coke and sludge in the conveyor-mixer is achieved by the rotation of two ribbon conveyors, set sufficiently close together so that flights of one revolve in the free space of the other. Hence thorough mixing of the coke and fresh sludge is obtained during the time they are being transported to a rotor-lift (D).

Coke-sludge mixture is fed by gravity to the rotor-lift and then transported vertically upward to the top of the retort, whence a horizontal conveyor carries the mixture to a heat exchanger (B), provided with 52 tubes which are hung freely from a tube sheet near the top of the exchanger shell. Coke flows down through these tubes, so being heated by the hot furnace gas circulating outside of the tubes. Coke falling from the tubes impinges on a conical baffle (X), which ensures even flow through all tubes of the exchanger. When the coke passes this cone it encounters the conveyor-mixer and there comes into contact with fresh sludge and so the cycle begins again.

Excess coke is removed at H and conveyed to a coke storage tank (K) which is air tight, then by conveyor (M) to storage bin (N).

No Contamination

Combustion gases cannot contaminate the SO_2 obtained as the flowing coke leaving the bottom of the heat exchanger acts as a seal preventing the gases from the exchanger from getting into and beyond the conveyor-mixer where the sulphur dioxide is evolved.

Hot air admitted to the tower part of the heat exchanger through pipe A heats the coke before it enters the conveyor-mixer. As a result of heating in the exchanger tubes and combustion with air, the coke particles leaving the heat exchanger have a temperature of between 450° and 650°F.

Considerable cracking of absorbed hydrocarbons takes place in the heat exchanger. The cracked hydrocarbons, as well as the gases which arise from the partial combustion of the coke, distill off. Part of this mixture of gases is then fed back to the furnace where additional fuel and air are introduced, when needed, to maintain the furnace exit gas at about 1400°F. Excess gas is bled off to a fume furnace (FF) where it is burnt in conjunction with natural gas.

Heat Input

Coke entering the conveyor-mixer must be sufficiently hot to furnish practically all the B.T.U.'s required to decompose the sludge which is admixed with it. Introduction of sludge in the conveyor-mixer reduces the coke temperature so that coke entering the bottom of the rotor-lift has a temperature of between 400°-500°F. The rotor-lift is jacketed and hot combustion gases pass within the jacket (I) to maintain the temperature of the coke. The horizontal conveyor (C) carrying the coke from the rotor-lift to the top of the heat exchanger is also well insulated.

The volume of coke is large in relation to the volume of sludge—as much as 30 tons of coke may be circulated with each ton of sludge.

Features of the Retort

Approximately 95% of the SO_2 content of the sludge is recovered in the retort. A prototype sludge (e.g. H_2SO_4 54%, water 8% and hydrocarbon 38%) used as feed yielded about 14 tons of coke for each 50 tons of sludge.

The retort is constructed of plain steel with the exception of the heat exchanger which is fabricated of stainless steel. The only severe corrosion takes place in the conveyor-mixer near where the sludge enters, and a portion of the ribbons on the screws has shown a tendency to wear out every four to six months.

Space requirement of a retort capable of processing 50 tons of sludge a day is as follows :—

	Width	Length	Height
Actual size (feet)	6	15	28
Size with working space (feet)	15	35	28

Cost of Retort

In practice the cost of the retort has proved somewhat higher than was first thought. A fair estimate is $175,000 for a 50-ton unit, exclusive of licence fee.

Operation of the retort is largely automatic, and one man can supervise the actual running of one to three retorts recording temperatures, adjusting sludge feed, etc.

Processing Refinery Acid Sludges using the Chemico Process

With Particular Mention to Dixon Chemical's Paulsboro Plant

Two major contracts have recently been awarded by the newly-formed Albatros Sulphuric Acid and Chemical Works at Vlaardingen, Holland, to Chemical Construction (G.B.) Ltd. (Chemico). The new company is owned jointly by Albatros Superfosfaatfabrieken N.V. of Utrecht, a member of the Royal Dutch Salt Group, and Cyprus Mines Corporation of Los Angeles. The projects which when installed will be valued at

£650,000, involve a large complex sulphuric acid contact installation of more than 100,000 tonnes (100% H_2SO_4) capacity a year, designed to use sulphur dioxide from roasting pyrites and from a Chemico designed plant for decomposing 56% sulphuric acid refinery sludge available from the adjacent Shell refinery.

Specific details of the sludge plant which is to be installed have not yet been released from Albatros. In as much as it will be based on the Chemico process it will have provision to burn the acid sludges together with additional sulphur, and fuel if needed, to produce SO_2. This gas stream is purified to remove acid mist, SO_3 and water and is then passed to a conventional sulphuric acid unit.

Variable Acid Feedstock

In the U.S., Chemico recently installed the world's largest sludge acid recovery plant for Dixon Chemical Industries Inc. at Paulsboro, New Jersey, to process acid sludges obtained from oil refineries. Nominal design capacity of this plant is 715 tons a day of 98% acid but the plant can operate at as low as 25% of capacity or as high as 120% of rated capacity. The acid feedstock can also vary from 90% H_2SO_4, 4% water and 6% hydrocarbon to only 75% H_2SO_4, 4% water and 21% hydrocarbons.

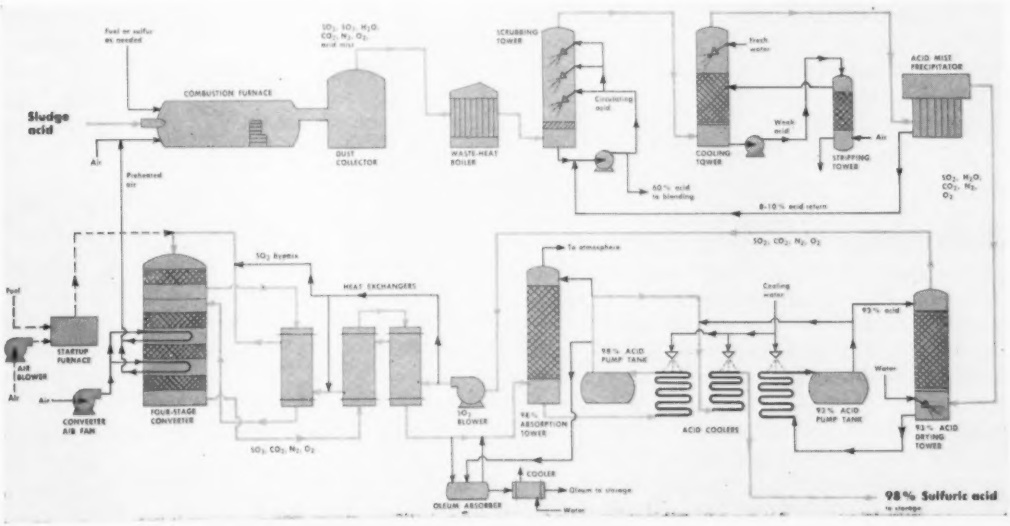
Low-acid sludges with high hydrocarbon content are obviously almost heat-sufficient for the burner reaction, but with the high-acid sludges some fuel oil or sulphur must be burned along with the sludge. Overall acid recovery from sludge at the Dixon plant averages 95%.

Plant Design

Through a spinning-cup burner acid sludge is injected into a 16ft. diameter burning chamber. Reaction temperature is from 2,000° to 2,300°F. To keep sulphur trioxide formation to a minimum, excess oxygen content is limited to 2% to 4% by regulation of air admitted to the burner.

From the burner, flame products pass to a dust-collecting chamber where larger ash particles are deposited. Gas then passes to a water-tube, waste-heat boiler where gas temperature drops to about 700°F. A rise in exit gas temperature denotes fouling due to depositing of ash on the boiler tubes, which have to be steam cleaned periodically.

From the waste-heat boiler, gas flows to a scrubber where SO_3 and acid mist is absorbed in 60% acid. In a second tower contacting cool water chills the gas to 105°F. An electrostatic precipitator operating at 80,000 volts



Chemico process for converting waste acid sludge acid to H_2SO_4 at Dixon Chemical Co.'s Paulsboro plant

removes any acid mist remaining which is recycled to the scrubbing tower.

Water vapour in the SO_2 is removed in a drying tower by contacting with 93% H_2SO_4, after which the SO_2 is passed through a 56,000 s.c.f.m. centrifugal blower with 4 p.s.i.g. pressure rise.

Dry SO_2 gas passes through three shell-and-tube heat exchangers where it is preheated against the hot SO_3 stream leaving the converter. The SO_2 stream enters the converter at about 820°F. After passing through the first layer of vanadium catalyst, gas temperature rises to about 1,100°F after about 75% of the SO_2 is converted to SO_3. The gas stream is then cooled to 830°F with the incoming SO_2; heat of reaction in the next two catalyst beds is removed by cold air circulating through hairpin coolers so that SO_3 stream is at about 825°F before passing through the heat-exchangers.

Cooled SO_3 enters the absorption tower to 325° to 357°F to contact 98% acid. Product acid from the absorber is cooled and sent to storage tanks. If required a 60% acid stream can be drawn from the bottom of the first scrubbing tower for blending with 98% acid stream to make 60° Be product. If oleum is wanted a sidestream of SO_3 can be converted and contacted with 98% acid in a small absorption tower, and 93% acid product can be obtained by withdrawing a stream from the bottom of the drying tower and pumping it through an air-stripping tower to recover any SO_2 dissolved in the acid.

Constructional Materials

Materials used in construction of the Dixon plant are of interest. The sludge burner comprises a steel shell lined with firebrick. There are three layers to the scrubbing tower and the gas-cooling tower — a steel outer shell lined with lead with an inner core of acid proof brick. The flue leading from the cooler to the mist precipitator is rubber-lined steel and tht precipitator itself is lead-lined, followed by a rubber-lined gas flue. Circulating acid lines and the gas flue from the top of the scrubber are made of Haveg to resist corrosion while gas flues in the rest of the plant are plain carbon steel. The converter is carbon steel and drying and absorption towers are steel, lined with acid-proof brick. Piping for 98% acid is cast iron.

The Dixon plant has other novel features. A blower-suction system is used up to the drying tower stage since a blower in contact with moist acidic gas is soon corroded away. After the drying tower stage, the gas is pulled through the 56,000 s.c.f.m. centrifugal blower with a 4 p.s.i.g. pressure rise. The heat exchangers, shell-and-tube type, have extra heat transfer surfaces and are heavily insulated to insure that at low flow rates the incoming SO_2 gas obtains enough pre-heat. It is also possible to install a small furnace and an additional heat exchanger at this point to supply the required heat at low flows.

Also, in view of the steadily mounting number of refineries now under construction and projected and the large amounts of waste acid sludges which will be to hand, this modernized process should have a considerable impact on the sulphuric acid industry.

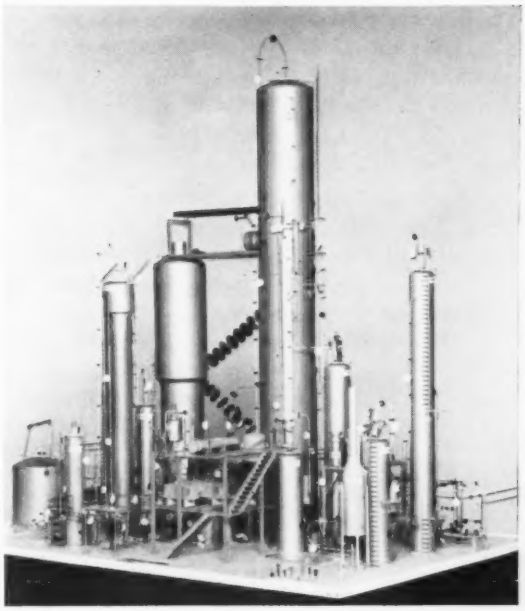
Anticaking Agent for Sulphur

POWDERS, such as sulphur, which tend to cake, can be transformed into smooth-flowing powders by the use of a superfine "airborne" silica-Cab-o-sil which has been developed by Minerals and Chemicals Division of Godfrey L. Cabot Inc., Boston, Massachussetts.

The silica is of exceptional purity (99.7%), has excellent hydrophilic properties, superfineness (11.114 per gramme), and an enormous external surface area (200 m^2/gm). In addition, it requires to be used in remarkably low concentrations. To give "caky" sulphur free-flowing properties, 9lbs. of Cab-o-sil is added per ton of sulphur (0.4%). Shaking suffices to ensure intimate mixing of the additive, which transforms the sulphur into a free-flowing powder. Cab-o-sil can also be used as a wetting agent. Ordinary sulphur, without the silica preparation, remains "caky" in water. When the silica is added free-flowing sulphur is stated to be dispersed instantly and thoroughly.

Desulphurisation of Industrial Gases using the Giammarco-Vetrocoke Process

Interest in Applications involving H_2S Removal Alone



Model of plant being installed in Japan

PROCESSES developed by Dr. Ing. Giammarco of Vetrocoke Azotati for the removal of CO_2 and H_2S from gas streams have achieved considerable success in recent years. Over 25 units have been installed and this world-wide interest is attributed to a number of advantages :—

- Selective removal of H_2S
- Possibility of operation over a wide range of pressures and temperatures
- Removal of CO_2 down to 0.5% and H_2S to less than 1 p.p.m. in a single stage
- Direct recovery of elemental sulphur as a by-product
- Freedom from corrosion
- Relative freedom from undesirable side reactions in the H_2S removal system
- Low capital and operating costs

The above points are of such importance that the G-V process is capable of very wide application including the removal of CO_2 and H_2S from natural gas, refinery tail gases and gas mixtures to be used for the synthesis of ammonia or methanol. Towns gas, whether derived from coal, coke or oil, may be treated for H_2S removal and various effluents such as sewage gas and contaminated air from viscose rayon spin baths offer a further field of application.

Most of the plants now in operation have as their chief function the removal of CO_2, although in some cases H_2S is also removed. There has been particular interest recently, however, in the possibility of applying the process to problems involving the removal of H_2S alone, and, in particular, the treatment of towns gas and waste gases. One plant is now in operation for the purification of towns gas and two others are in course of erection. Two plants are also being installed for the removal of H_2S from viscose rayon spin bath effluent gas.

Earliest work with the G-V liquid washing process, which was developed at the Porto Marghera works of Vetrocoke Azotati, was concerned with a type of hot potassium carbonate system. This was later improved by the use of solutions containing various organic activators. The use of carbonate solution containing arsenic was patented in 1954 and this patent forms the basis of the process which is now offered by various licensees in all parts of the world, including the Power-Gas Corporation Limited.

Although "a process" has been referred to, it should be made clear that the type of plant and the composition of the absorbing solution depend on the particular application. It is not, therefore, possible to describe a single plant

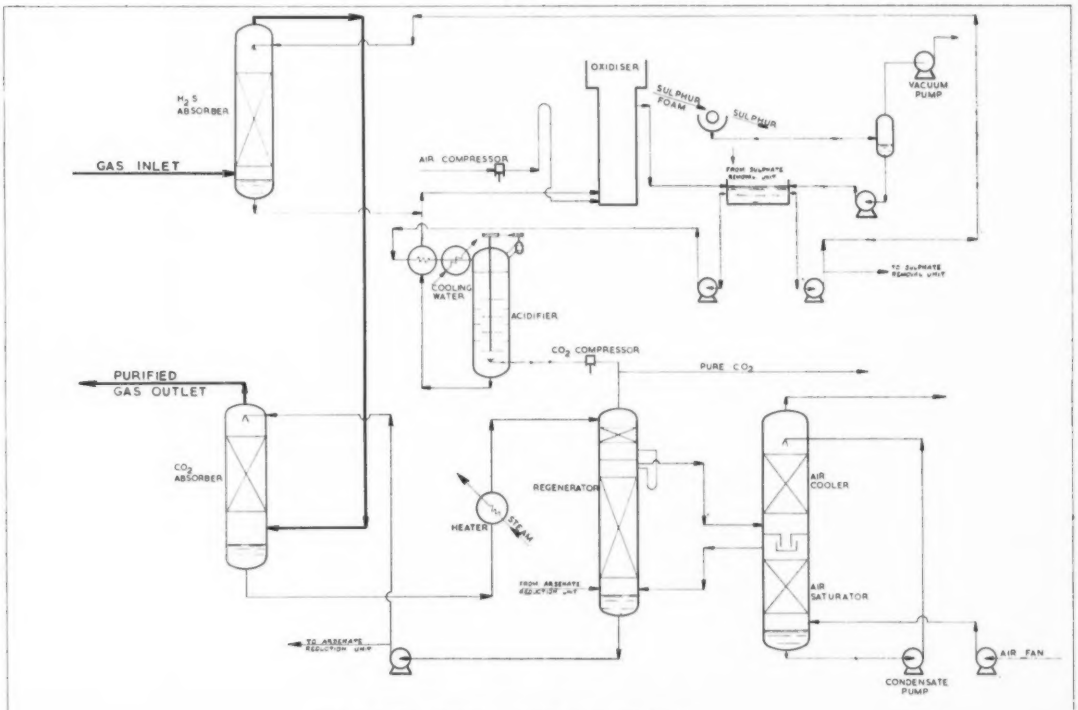
which would be generally applicable. The flow diagram below does, however, show a fairly standard type of plant for cases where both CO_2 and H_2S are to be removed, although H_2S alone can be removed from a gas stream containing both acid gases.

As far as the main gas stream is concerned, the process as indicated below is very simple. The gas stream passes through H_2S and CO_2 absorbers in series. The H_2S can readily be reduced to less than 1 p.p.m. while the CO_2 is generally reduced to about 0.2 to 0.5% depending upon the pressure of the gas. Lower CO_2 figures can be obtained, if economically justified.

Use of Arsenite

The chemistry of the CO_2 removal process is comparatively simple, the net effect being the absorption of CO_2 in potassium arsenite to give bicarbonate and arsenious oxide, which reaction is reversed in the regeneration system.

A number of complex reactions take place during H_2S absorption and oxidation, the main feature of the absorption being the production of mono-thio-arsenate, which is the characteristic compound of the G-V process. Other, apparently similar, processes result in the formation of higher thioarsenates which are more prone to side reactions and have higher H_2S partial pressures. Lowering the pH of the solution containing mono-thio-arsenate results in decomposition to elemental sulphur and arsenite. This lowering of the pH may be achieved by bubbling CO_2 through the solution or by oxidising arsenite in the solution to arsenate by an air stream. The flow diagram below and the following description refer to a unit using CO_2 for acidification. A simpler unit can use air. The use of CO_2 would be appropriate where an ammonia synthesis gas stream (available at elevated temperature) is



H_2S AND CO_2 REMOVAL BY THE G.V. PROCESS

being treated and a high pH solution used for absorption. The use of the acid gas CO_2, is, therefore, necessary for lowering the pH sufficiently to allow decomposition of the monothio-arsenate. Where H_2S only is to be removed from a cold gas such as coke oven gas or contaminated air, then a lower pH absorbent is employed. In this case the acidifier is unnecessary and the simpler unit is used. A separate acidifier is also unnecessary where CO_2 is to be removed from a gas stream at 40-50°C and where the CO_2 partial pressure is about four atmospheres.

The following description refers to the plant on the flow diagram.

The absorbing solution in the H_2S unit is pumped from a buffer tank to the absorption tower. After absorption the solution flows to the oxidiser and from the oxidiser back to the buffer tank. A second stream of liquor is taken from the buffer tank and cooled before passing to the acidifier. Elemental sulphur is formed in the acidifier and the suspension is returned to the oxidiser, where the sulphur is removed by froth flotation.

Acidification with CO_2 is carried out under pressure and at a temperature of 40-45°C so that the alkali is converted to bicarbonate. This lowering of the pH promotes the precipitation of sulphur.

Sulphur Flotation

Flotation of the sulphur and restoration of the arsenate-arsenite balance are carried out in the oxidiser tower. The tower is open to the atmosphere and is supplied with a stream of air at a velocity sufficient to float the sulphur. The sulphur foam may be filtered by means of a rotary vacuum filter or filter press and washed with condensate. The filter cake can conveniently be reduced to about 50% moisture and when dry contains an arsenic content (in the form of arsenite or thioarsenate) of less than 0.3%. If required, the sulphur may be further purified by solvent extraction.

During operation there is a certain build-up of sulphate in the solution and if cyanides are present a certain amount of thiocyanate must be removed. It must be emphasized, however, that in the G-V process these side reactions are kept down to a very considerable extent, in fact, it has been shown at the Porto Marghera plant, that when starting a unit with new solution, it is unnecessary to use the treatment unit until after about 12 months' operation. This treatment unit consists of an autoclave for destruction of thiocyanates and a concentrator and precipitation vessel to remove sulphate.

In the CO_2 removal unit the absorbing solution is pumped to the absorber from the base of the regenerator tower, and then flows under absorber pressure back to the top of the regenerator. The diagram shows a plant for recovery of about 30% CO_2, but higher recoveries of CO_2 are possible, steam regeneration being essential for recoveries of 80-100%. The solution from the absorber is heated in a steam heater and CO_2 is flashed in the top section of the regenerator. The solution from the flash vessel then flows under gravity into the air regenerator where it is stripped in countercurrent. A saturater-cooler system operating between the inlet air and the effluent air-CO_2 mixture is used to minimise the heat consumption of the stripping process. In order to keep down the concentration of arsenate in the solution, a side stream is taken to a small autoclave where arsenate is reduced to arsenite.

Removal of CO_2 and H_2S by the G-V process is becoming of considerable importance in the synthetic ammonia field and in this connection attention is drawn to a plant to be erected in Japan (a model of this plant is illustrated). This model includes both H_2S and CO_2 removal systems and a CO conversion unit. In comparison there is the H_2S removal unit at Porto Marghera, which has been in operation for a number of years. The simplicity of the plant is noteworthy.

Capital and Operating Costs

A claim of low capital and operating costs has been made earlier in this article. It is extremely difficult to give genuine comparative figures for different processes for CO_2 and H_2S removal since operating conditions, feed gas analyses and product requirements are not easily equated and it is in fact impossible to choose conditions which would enable a fair appraisal to be made. In practice the particular conditions determine the choice of process, but experience has shown that over a very wide range the G-V process has definite advantages.

An actual example of this was given in preparing a scheme for CO_2 removal in a large works where it was intended to separate hydrocarbons at a later stage. It appeared likely that CO_2 removal by means of monoethanolamine might be suitable and a cost comparison was, therefore, made against the G-V. process with the following results:—

Conditions	2,650,000 NCFH gas at 375 p.s.i. and 100°F CO_2 content to be reduced from 15.6% to 0.5%.
Capital Costs	MEA Unit £430,000 G.V Unit £300,000

Utility costs per day

	MEA	G-V
Steam	£1,750	£300
Power	£ 4	£ 55
Water	£ 740	£ 43
Condensate	—	£ 38
Chemicals	£ 10	£ 3
	£2,504	**£439**

The above figures are, of course, approximate and should be considered with due caution, the differences, however, are so large that there can be no doubt that the G-V process offers very substantial financial advantages.

Transwestern Pipeline Co. has First U.S. G-V installation

Now in commercial operation is the first plant in the Western Hemisphere to use the Giammarco-Vetrocoke process to sweeten gas. Transwestern Pipeline Company has installed the G-V plant at its Pickett gas field about 35 miles from Fort Stockton, Texas. Designed and built by Brown and Root Inc., this latest plant is the largest of the 20-odd G-V units throughout the world. It can sweeten 180 m.s.c.f.d. of Transwestern Pipeline's output before the gas enters their new 1500-mile pipeline for transporting Texas natural gas to California, reducing CO_2 content from 28% to under 2% and removing most of the gases' 0.2% H_2S.

Plant Design

As designed by Brown and Root the facility has parallel trains of equipment so that operation can be adjusted for fluctuations in pipeline gas demand. Metallic salts (unspecified) are used as activators and solutions are regenerated with air.

No comparative figures are available at the moment for H_2S removal alone, but it is hoped that such figures may be presented at a later date. Summarising the position, however, it is fair to say that the G-V process has firmly established itself as an attractive standard process for CO_2 and H_2S removal and that in the future greater inteerst is expected in industries concerned solely with H_2S removal.

LICENSEES OF THE G.-V PROCESS

England
Humphreys & Glasgow—London
Simon-Carves—Stockport
Power-Gas—Stockton-on-Tees
Coppee Company—London
U.S.A.
Fluor Corp.—Los Angeles
C. F. Braun—Alhambra
Brown & Root—Houston, Texas
Bechtel Corp.—S. Francisco
Blaw-Knox—Pittsburgh
Belgium
Evence Coppee—Bruxelles
France
Compagnie de Fours—Montrouge
Soc. Auxiliaire Thermochimique—Paris
Heurtey—Paris
Germany
Pintsch Bamag—Butzbach
Otto—Bochum
Bischoff—Essen
Baumco—Essen
Lurgi—Frankfurt
Holland
Comprimo N.V.—Amsterdam
Italy
Ammonia Casale—Rome
Gas Integrale—Milan
Siry Chamon—Milan
Montecatini—Milan
Japan
Chiyoda Chem. Eng. Constr.—Chiyoda-Ku-Tokyo

Fee gas enters at 1,050 p.s.i.g., and a dry-type separator removes liquid hydrocarbons. The gas is then heated and enters an absorption tower for H_2S removal, where it passes upward through a packed bed in countercurrent to the treating solution. Then carbon dioxide is removed in packed-bed contactors. The gas which emerges contains under 0.25 grains H_2S/100 cu. ft. and less than 6lb. water/million cu. ft.

Spent Solution

Spent solution from the H_2S absorbers passes to flotation towers, part of it passing through digesters for acidification by CO_2. In the flotation towers sulphur removal is effected by air, the sulphur being carried to the top of the tower and the solution is reactivated. The foam is settled and filtered, and the filtrate combined with the solution leaving the bottom of the tower, returns to the H_2S absorbers. Sulphur cake from the filter goes to a water-wash tank, and is then refiltered.

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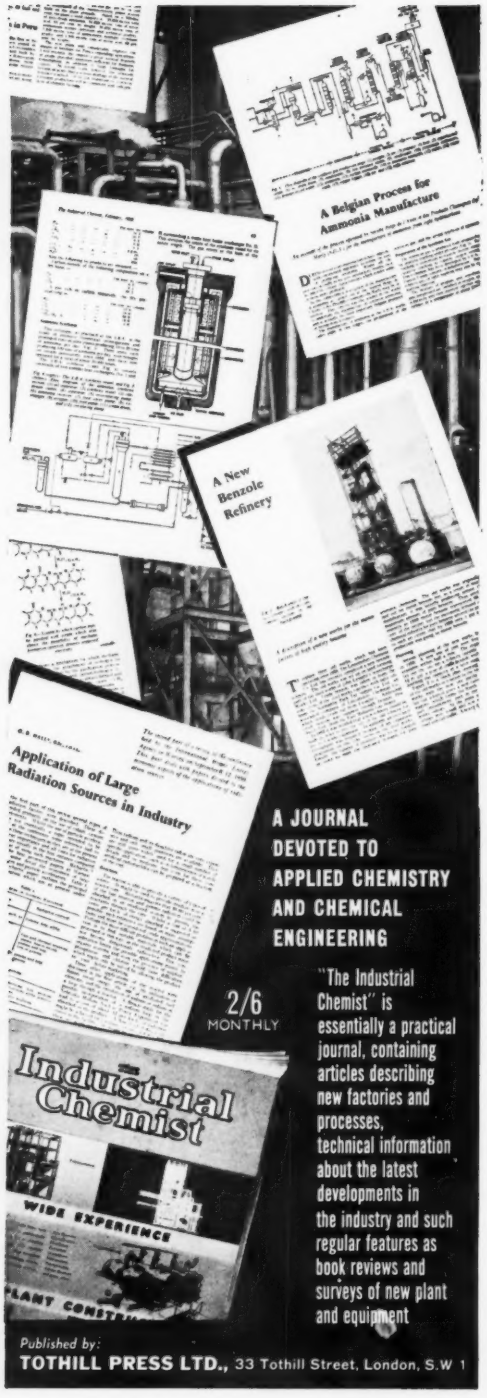
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